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(54) Process for isomerizing linear olefins to isoolefins.

(57) This invention provides a process to convert linear alkenes such as butene-1 and butene-2 to methyl branched chain alkenes such as isobutylene using one dimensional, medium pore zeolite catalysts and similar type catalysts such as SAPO's and MeAPOS's. The pore size for the catalyst should be greater than 0.42 nm and less than 0.7 nm, preferably with a larger dimension of between 0.5 and 0.6 nm. This pore size allows the branched chain alkenes to form and diffuse out of the catalyst while reducing the formation of unwanted by-products, including dimers, trimers, aromatics and coke. This invention has been demonstrated with H-ferrierite, SAPO-11, and magnesium mordenite in a laboratory scale reactor. Selectivities ranging from about 50% to almost 100% were demonstrated for isobutylene formation using H-ferrierite, at temperatures ranging from about 340°C to about 440°C.

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This invention relates to structural isomerization of linear olefins to methyl branched isoolefins using zeolite compositions as isomerizing catalysts.

Increasing demand for high octane gasoline blended with lower aliphatic alkyl ethers such as octane boosters and supplementary fuels has created a significant demand for isoalkylethers, especially the C₅ to C₇ methyl, ethyl and isopropyl-t-alkyl ethers. Consequently, there is an increasing demand for the corresponding iso-alkene starting materials such as isobutene, isoamylenes and isohexenes.

In many instances, it is desirable to convert an alkene such as normal butene, to a methyl branched alkene, for example isobutylene, by mechanisms such as structural isomerization. Such converted isoalkenes then can be reacted further, such as by polymerization or oxidation, to form useful products. Normal alkenes containing four carbon atoms (1-butene, trans-2-butene and cis-2-butene) and five carbon atoms (1-pentene, trans-2-pentene, and cis-2-pentene) are relatively inexpensive starting compounds. Conventionally, butenes and amylenes, including to a minor extent isobutylene and isoamylene, are obtained as a by-product from refinery and petrochemical processes such as catalytic and thermal cracking units.

Zeolite materials, both natural and synthetic, are known to have catalytic properties for many hydrocarbon processes. Zeolites typically are ordered porous crystalline aluminosilicates having a definite structure with cavities interconnected by channels. The cavities and channels throughout the crystalline material generally can be of such a size to allow selective separation of hydrocarbons. Such a hydrocarbon separation by the crystalline aluminosilicates essentially depends on discrimination between molecular dimensions. Consequently, these materials in many instances are known in the art as "molecular sieves" and are used, in addition to catalytic properties, for certain selective adsorptive processes. Zeolite molecular sieves are discussed in great detail in D.W Breck, Zeolite Molecular Sieves, Robert E. Krieger Publishing Company, Malabar, Florida (1984).

Generally, the term "zeolite" includes a wide variety of both natural and synthetic positive ion-containing crystalline aluminosilicate materials, including molecular sieves. They generally are characterized as crystalline aluminosilicates which comprise networks of SiO₄ and AlO₄ tetrahedra in which silicon and aluminum atoms are cross-linked in a three-dimensional framework by sharing of oxygen atoms. This framework structure contains channels or interconnected voids that are occupied by cations, such as sodium; potassium, ammonium, hydrogen, magnesium, calcium, and water molecules. The water may be removed reversibly, such as by heating, which leaves a crystalline host structure available for catalytic activity. The term "zeolite" in this specification is not limited to crystalline aluminosilicates. The term as used herein also includes silicoaluminophosphates (SAPO), metal integrated aluminophosphates (MeAPO and ELAPO), metal integrated silicoaluminophosphates (MeAPSO and ELAPSO). The MeAPO, MeAPSO, ELAPO, and ELAPSO families have additional elements included in their framework. For example, Me represents the elements Co, Fe, Mg, Mn, or Zn, and El represents the elements Li, Be, Ga, Ge, As, or Ti. An alternative definition would be "zeolitic type molecular sieve" to encompass the materials useful for this invention.

Developments in the art have resulted in formation of many synthetic zeolitic crystalline materials. Crystalline aluminosilicates are the most prevalent and, as described in the patent literature and in the published journals, are designated by letters or other convenient symbols. Zeolites have been specifically named and described as Zeolite A (U.S. Patent No. 2,882,243), Zeolite X (U.S. Patent No. 2,882,244), Zeolite Y (U.S. Patent No. 3,130,007), Zeolite ZSM-5 (U.S. Patent No. 3,702,886), Zeolite ZSM-11 (U.S. Patent No. 3,709,979), Zeolite ZSM-12 (U.S. Patent No. 3,832,449), Zeolite ZSM-23 (U.S. Patent No. 4,076,842), Zeolite ZSM-35 (U.S. Patent No. 4,016,245), Zeolite ZSM-48 (U.S. Patent No. 4,375,573), Zeolite NU-1 (U.S. Patent No. 4,060,590) and others. Various ferrierite zeolites, including the hydrogen form of ferrierite, are described in U.S. Patent Nos. 3,933,974, 4,000,248 and 4,942,007 and patents cited therein. SAPO-type catalysts are described in U.S. Patent No. 4,440,871. MeAPO type catalysts are described in U.S. Patent Nos. 4,544,143 and 4,567,029; ELAPO catalysts are described in U.S. Patent No. 4,500,651, and ELAPSO catalysts are described in European Patent Application 159,624.

Up until now, catalysts for structurally isomerizing alkenes, particularly butene to isobutene, have utilized large pore zeolites having two or three-dimensional interconnecting channels, together with an associated catalytic metal such as platinum, palladium, boron or gallium. Continuing problems with present methods using such zeolites are coking of the catalyst pore spaces and undesirable by-product formation, in particular dimers, trimers and aromatics.

SUMMARY OF THE INVENTION

In the methods of this invention, a linear olefin is converted under isomerizing conditions to a methyl branched olefin using an isomerizing catalyst composition made up of a zeolite having only in one dimension a pore structure having a pore size small enough to retard by-products and retard the formation of coke and

its precursors and large enough to permit entry of the linear olefin and diffusion of the isoolefin product. Generally, zeolites having in one dimension a pore structure with a pore size ranging from more than about 0.42 nm to less than about 0.7 nm are useful for the processes of this invention. Zeolites with this specified pore size are typically referred to as medium or intermediate pore zeolites and typically have a 10-member (or puckered 12-member) ring channel structure in one dimension and an 8-member or less (small pore) in the other dimensions, if any. For purposes of this invention, a one-dimensional pore structure is considered one in which the channels having the desired pore size do not interconnect with other channels of similar or larger dimensions; it may also be considered alternatively as a channel pore structure (see U.S. Patent No. 3,864,283) or uni-directional sieve. Such one-dimensional, intermediate pore size catalyst compositions provide increased selectivity of the isomerization reaction, decreased dimer and trimer by-product formation, and decreased coking of the catalyst.

Zeolites that contain small pores (i.e., less than about 0.42 nm) do not allow for diffusion of the methyl branched isoolefin product, e.g., isobutylene; while zeolites that contain large pores (i.e., greater than about 0.7 nm) in any one dimension are subject to substantial by-product formation and coking. Coking is believed to be the result of oligmerization and polymerization, aromatization, or alkylation of the feed paraffin or olefin hydrocarbons. Zeolites of this invention should contain at least one pore dimension with the specified pore size. A two or three-dimensional pore structure having the specified pore size would permit substantial contact of the isomerizing olefins and thereby facilitate unwanted dimerization and trimerization reactions.

The processes of this invention are characterized by selectivities which range from about 50 % to 99 % over run lengths of 48 to 120 hours, and isoolefin yields of between about 25% to 40% at the beginning of a run and 12% to 40% at the end of run conditions. Under preferred conditions with temperatures at least about 370°C, selectivities generally exceed 70% over run lengths of 48 to 120 hours.

Lower temperatures, such as in the range of 340°C to about 370°C at WHSV of about 2 to about 5 hr⁻¹, and at atmospheric pressures, generally yield lower selectivities, but yet still provide unexpectedly good selectivities ranging from about 50 % to 65 % for run lengths of about 50 to about 70 hours.

Further, use of catalysts made with pressed zeolite powders of various silica to alumina ratios, without added binders, show dramatically improved yields over time as compared to similar catalysts made with binders.

BRIEF DESCRIPTION OF THE DRAWINGS

FIG. 1 is a graph of isobutylene conversion and selectively versus run time illustrative of a process of this invention, utilizing an H-ferrierite catalyst at 440°C, WHSV of 7 hr⁻¹, and at about atmospheric pressure.

FIG. 2 is a graph of isobutylene yield versus run time illustrative of a process of this invention, utilizing an H-ferrierite catalyst at 440°C, WHSV of 7 hr⁻¹, and at about atmospheric pressure.

FIG. 3 is a graph of isobutylene conversion and selectivity versus run time illustrative of a process of this invention, utilizing an H-ferrierite catalyst, at 340°C, WHSV of 4.5 hr⁻¹, and at about atmospheric pressure.

FIG. 4 is a graph of isobutylene yield over run time illustrative of a process of this invention, utilizing an H-ferrierite catalyst, at 340°C, WHSV of 4.5 hr⁻¹, and at about atmospheric pressure.

FIG. 5 is a graph of isobutylene conversion and selectivity versus run time illustrative of a process of this invention, utilizing a pressed H-ferrierite powder catalyst, at 430°C, WHSV of 7 hr⁻¹, and 18.7 psia.

FIG. 6 is a graph of isobutylene yield over run time illustrative of a process of this invention, utilizing a pressed H-ferrierite powder catalyst, at 430°C, WHSV of 7 hr⁻¹, and 18.7 psia.

FIG. 7 is a schematic flow scheme of a process of this invention.

DETAILED DESCRIPTION OF THE PREFERRED EMBODIMENTS

Hydrocarbon Feed Stream

The hydrocarbon feed useful for this invention comprises a substantially linear alkene. Typically, the linear alkene will contain four to ten carbon atoms. Also considered a linear alkene for purposes of this invention is a compound containing a linear alkene segment with four to ten carbon atoms. It is believed that long chain linear alkenes and compounds containing long chain linear segments may penetrate the zeolite catalyst for a distance effective to allow isomerization. Thus, the entire molecule need not be small enough to fit entirely within the pore structure of the catalyst. The preferred feed contains butylene or amylyene.

As used herein, n-butylene includes all forms of n-butylene, for example 1-butene and 2-butene, either trans-2-butene or cis-2-butene, and mixtures thereof. As used herein, n-amylyene or n-pentene, includes 1-pentene, cis- or trans-2-pentene, or mixtures thereof. The n-butylene or n-amylyene used in the processes of this invention is generally in the presence of other substances such as other hydrocarbons. Thus, a feedstream

used in the process of the invention containing n-butylene or n-amylene also can contain other hydrocarbons such as alkanes, other olefins, aromatics, hydrogen, and inert gases. Typically, the n-butene feedstream used in this invention contains about 40 to about 100 wt. % n-butene. For example, a hydrocarbon feedstream from a fluid catalytic cracking effluent stream generally contains about 40 to about 60 wt. % normal butene and a hydrocarbon effluent from an ether processing unit, such as a methyl-tert-butyl ether (MTBE) processing unit generally containing from 40 to about 100 wt. % n-butylene.

As used herein, the term "alkene" can be alternatively referred to as "olefin"; the term "linear" can be alternatively referred to as "normal"; and the term "isoolefin" can be alternatively referred to as "methyl branched isoolefin." Similarly, butene and butylene refer to the same four carbon alkene; and pentene and amylene refer to the same five carbon alkene.

Isomerizing Catalyst

The zeolite catalyst useful in the processes of this invention comprises a zeolite having one-dimensional pore structures with a pore size ranging from greater than about 0.42 nm and less than about 0.7 nm. The zeolite catalyst preferably comprises substantially only zeolites with the specified pore size in one dimension. Zeolites having pore sizes greater than 0.7 nm are susceptible to unwanted aromatization, oligimerization, alkylation, coking and by-product formation. Further, two or three-dimensional zeolites having a pore size greater than 0.42 nm in two or more dimensions permit dimerization and trimerization of the alkene. Hence, zeolites having a pore diameter bigger than about 0.7 nm in any dimension or having a two or three-dimensional pore structure in which any two of the dimensions has a pore size greater than about 0.42 nm are excluded as part of this invention.

Examples of zeolites that can be used in the processes of this invention, which have one-dimensional pore structures with a pore size between about 0.42 nm and 0.7 nm, include the hydrogen form of ferrierite, SAPO-11, SAPO-31, SAPO-41, FU-9, NU-23, NU-10, ZSM-12, ZSM-22, ZSM-23, ZSM-35, ZSM-48, ZSM-50, MeAPO-11, MeAPO-31, MeAPO-41, MeAPSO-11, MeAPSO-31, and MeAPSO-41, ELAPO-11, ELAPO-31, ELAPO-41, ELAPSO-11, ELAPSO-31, and ELAPSO-41, laumonite, clinoptilolite, cancrinite, offretite, hydrogen form of heulandite, hydrogen form of stilbite, and the magnesium or calcium form of mordenite. The isotopic structures of these frameworks, known under other names, are considered to be equivalent. An overview describing the framework compositions of many of these zeolites is provided in New Developments in Zeolite Science Technology, "Aluminophosphate Molecular Sieves and the Periodic Table," Hanigen et al. (Kodansha Ltd., Tokyo, Japan 1986).

Many natural zeolites such as ferrierite, heulandite and stilbite feature a one-dimensional pore structure with a pore size slightly smaller than the desired 0.42 nm diameter. These same zeolites can be converted to zeolites with larger pore sizes by removing the associated alkali metal or alkaline earth metal by methods known in the art, such as ammonium ion exchange, optionally followed by calcination, to yield the zeolite in its hydrogen form. See e.g., U.S. Patent Nos. 4,795,623 and 4,942,027 incorporated herein by reference. Replacing the associated alkali or alkaline earth metal with the hydrogen form correspondingly enlarges the pore diameter. It is understood that the pore diameter or "size" shall mean the effective pore diameter or size for diffusion. Alternatively, natural zeolites with too large a pore size, such as mordenite, can be altered by substituting the alkali metal with larger ions, such as larger alkaline earth metals to reduce the pore size and thus become useful for the processes of this invention.

Exemplary of zeolites that are not useful for the processes of this invention include ZSM-5, erionite, zeolite Y, hydrogen form of mordenite, and faujasite.

The zeolite catalyst used in the isomerization processes of this invention can be used alone or suitably combined with a refractory oxide that serves as a binder material. Suitable refractory oxides include natural clays, such as bentonite, montmorillonite, attapulgite, and kaolin; alumina; silica; silica-alumina; hydrated alumina; titania; zirconia and mixtures thereof. The weight ratio of binder material and zeolite suitably ranges from 1:9.5 to 9:1, preferably 1:4.

Catalytic compositions comprising the crystalline zeolite material of the invention and a suitable binder material can be formed by blending a finely divided crystalline zeolite with a binder material. The resulting mixture is thoroughly blended and mulled typically by adding water and/or a volatizable acidic material such as nitric acid or acetic acid. The resulting gel can be dried and calcined, for example, at temperatures between about 450°C and 550°C, preferably between about 500°C and 520°C, to form a composition in which the crystalline zeolite is distributed throughout the matrix of binder material. Additionally, the catalyst composition can be extruded to form pellets, cylinders, or rings, or shaped into spheres, wagon wheels or polylobe structures.

H-Ferrierite Catalyst

H-ferrierite is the preferred zeolite catalyst for use in the isomerization processes of this invention. H-ferrierite is derived from ferrierite, a naturally occurring zeolite mineral having a composition varying somewhat with the particular source. A typical elemental composition of ferrierite is



The prominent structural features of ferrrierite found by x-ray crystallography are parallel channels in the alumino-silicate framework. These channels, which are roughly elliptical in cross-section, are of two sizes: larger channels having major and minor axes of 5.4 and 4.2 Å, respectively, and smaller parallel channels having major and minor axes of 4.8 and 3.5 Å, respectively. Conversion of ferrierite to its hydrogen form, H-ferrierite, replaces sodium cations with hydrogen ions in the crystal structure. Both the alkali metal and hydrogen forms reject multiple branched chain and cyclic hydrocarbon molecules and retard coke formation. According to the purposes of this invention, H-ferrierite is considered to be comprised substantially of a one-dimensional pore structure having an elliptical pore size (> 0.54 nm and > 0.42 nm) large enough to permit entry of the linear olefin and diffusion of the methyl branched isooolefin and small enough to retard coke formation. The one-dimensional feature is satisfied because there are no other interconnecting channels which have diameters similar to or greater than the primary (> 0.54 nm and > 0.42 nm) channel.

Various methods are provided which teach procedures for preparing H-ferrierite, including U.S. Patent Nos. 4,251,499, 4,795,623 and 4,942,027, incorporated herein by reference. In making the H-ferrierite, the H-ferrierite will typically have a silica (SiO_2):alumina (Al_2O_3) molar ratio of greater than about 5:1, suitably have a ratio of between 5:1 and 500:1, desirably have a ratio between about 5:1 and about 300:1 and preferably have a ratio of between about 10:1 and about 100:1.

H-Ferrierite Catalyst No. 1

A hydrogen exchanged ferrierite powder with a molar silica (SiO_2) to alumina (Al_2O_3) ratio of about 19, a sodium content less than 0.01 wt.% and a surface area of 420 square meters/gram was used to prepare the catalyst. The framework of this zeolite contained both 8 and 10 T-atom rings arranged as described on pages 64 and 65, of the book "Atlas of Zeolite Structure Types" by W.M. Meier and D.H. Olson, Butterworths, 2nd Edition, 1987. The pore dimensions of the 8 and 10 T-atom rings in this H-ferrierite are slightly larger than 3.5 Å x 4.8 Å and 4.2 Å x 5.4 Å, respectively. Not including the microporosity of the zeolite, the finished catalyst pore size distribution by mercury intrusion was bi-modal in nature with peaks at approximately 35 and 1150 angstroms. This H-ferrierite powder was extruded with alumina and calcined at 500°C to produce 1/16" cylinders of a H-ferrierite catalyst with the following measured physical properties.

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	Loss On Ignition @ 1100°C	6.7 wt%
	SiO_2 (anhydrous w/o binder)	91.7 wt%
	Al_2O_3 (anhydrous w/o binder)	8.5 wt%
40	Na_2O	0.01 wt%
	CaO	0.01 wt%
	MgO	0.01 wt%
	Fe_2O_3	0.05 wt%
45	Compacted Bulk Density (finished catalyst)	40 lb/ft ³
	Surface Area (zeolite powder, P/Po)	420 m ² /gram
50	Surface Area (finished catalyst)	376 m ² /gram
	Binder	20 wt%

H-Ferrierite Catalyst No. 2

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The H-ferrierite powder as described above ($\text{SiO}_2/\text{Al}_2\text{O}_3 = 19$), without added binder, was pressed, crushed and sieved into 6-20 mesh particles. The particles were then calcined for two hours at 500°C to produce a catalyst with the measured physical properties listed in Table 1.

H-Ferrierite Catalyst No. 3

5 Hydrogen exchanged ferrierite with a molar silica to alumina ratio of 42 ($\text{SiO}_2/\text{Al}_2\text{O}_3 = 42$), was pressed, crushed and sieved into 6-20 mesh particles. The particles were then calcined for two hours at 500°C to produce a catalyst with the measured physical properties listed in Table 1.

H-Ferrierite Catalyst No.4

10 Hydrogen exchanged ferrierite with a molar silica to alumina ratio of 87 ($\text{SiO}_2/\text{Al}_2\text{O}_3 = 87$), was pressed, crushed and sieved into 6-20 mesh particles. The particles were then calcined for two hours at 500°C to produce a catalyst with the measured physical properties listed in Table 1.

H-Ferrierite Catalyst No. 5

15 Potassium/Sodium ferrierite with a molar silica to alumina ratio of 16 ($\text{SiO}_2/\text{Al}_2\text{O}_3 = 16$) was obtained from TOSOH Corporation. The K/Na-ferrierite was converted into the ammonium form by ammonium ion exchange. After washing and drying, the NH_4^+ -ferrierite powder was pressed, crushed and sieved into 6-20 mesh particles. The particles were then calcined for two hours at 500°C.

H-Ferrierite Catalyst No. 6

20 H-ferrierite catalyst powder ($\text{SiO}_2/\text{Al}_2\text{O}_3 = 19$) as described above was combined with 20 wt.% silica binder (silica grade 951 obtained from W.R. Grace Co.). The mixture was pressed, crushed and sieved into 6-20 mesh particles. The resulting particles exhibited a higher crush strength than the pressed zeolite material alone, i.e.,
25 H-ferrierite catalyst No. 2.

TABLE 1

30 PHYSICAL PROPERTIES OF THE
CATALYSTS NO. 1 THROUGH 6

		1	2	3	4	5	6
35	H-Ferrierite $\text{SiO}_2/\text{Al}_2\text{O}_3$	19	19	42	87	16	19
40	Sodium (ppm)	42	32	700	300	150	83
	Surface Area (m^2/g)	376	404	222	326	323	415
45	Binder Content (wt. %)	20	0	0	0	0	20
		=====	=====	=====	=====	=====	=====

Isomerizing Conditions

50 In the processes of this invention, a hydrocarbon stream comprising a linear olefin is contacted with the catalytic zeolite under isomerizing conditions. Generally, in the processes of this invention, the hydrocarbon stream is contacted with the above-described zeolite catalyst in a vapor phase at a suitable reaction temperature, pressure and space velocity. Generally, suitable reaction conditions include a temperature of about 250°C to about 650°C, more typically from about 340°C to about 600°C, an olefin partial pressure of above about 0.5 atmosphere, and a total pressure of about 0.5 to about 10.0 atmospheres or higher, a hydrogen/hydrocarbon molar ratio of 0 to about 30 or higher, substantially free of water (i.e., less than about 2.0 wt% of the feed), and a hydrocarbon weight hourly space velocity (WHSV) of about 1.0 to about 50 hr⁻¹. The hydrogen can be
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added directly to the feed stream prior to introduction of the isomerization zone, or the hydrogen can be added directly to the isomerization zone. In a typical process scheme, an olefin-containing hydrocarbon vapor stream is contacted with such catalyst in a reactor at about 340°C to about 475°C, at an olefin partial pressure of about 10 psia to about 20 psia and a total pressure of about 15 to about 30 psia, without added hydrogen, and at a hydrocarbon based WHSV of about 2 to about 28 hr⁻¹. Preferred isomerizing conditions are carried out at a temperature of between about 370°C to 440°C, at atmospheric pressures, and a hydrocarbon based WHSV of between about 7 to about 15 hr⁻¹.

The process according to the present invention can be carried out in a packed bed reactor, a fixed bed, fluidized bed reactor or a moving bed reactor. The bed of the catalyst can move upward or downward.

During the process, some coke will be formed on the catalyst. Therefore, it is advantageous to regenerate the catalyst. The catalyst can be regenerated by subjecting it to heat treatment with air, nitrogen/oxygen gas mixture, or hydrogen. A continuous regeneration, similar to the regeneration carried out in a fluidized catalytic cracking process may be useful.

The performance of the zeolite catalyst can be affected by controlling the water content in the catalyst. Water content of the catalyst can be adjusted by methods such as adding water to the feed or by directly adding water to the reactor. Calcination conditions will also affect the water content of the catalyst. These methods are referred to as controlled hydration of the catalyst.

Description of the Testing Apparatus

The laboratory pilot unit was a semi-automated unit that can control flow, temperature, and pressure. It can also collect samples for analysis and record process variable data. The process variable data was collected with an analog to digital (A to D) input/output converter. The A to D converter was connected to a personal computer (PC) which runs a process control software package. This software package allowed the operator to monitor the process variable data and control the unit using proportional/integral/derivative (PID) control blocks for flow and pressure. It also archived the process variable data on magnetic media.

The pilot reactor occupied three separate hoods: The feed hood contained the feed system where the feed was stored in a five-gallon cylinder. The feed tank rested on a load cell that was used to monitor the weight of the feed cylinder. The feed tank was pressurized with a 60-80 psig nitrogen blanket. This nitrogen pressure fed the hydrocarbon feed containing butylenes to the system. The feed flow rate was controlled by PID control block in the process control software. This control block consisted of two flow meters, an instrument to pneumatic signal converter, and a flow control valve located downstream of the flow meters. The two flow meters were used independently and were calibrated for different flow rate ranges. The feed system also had an additional connection for bottled gas addition or water injection with the feed.

The reactor hood contained the reactor and heating furnace. The reactor was a 2 inch o.d. and 1.6 inch i.d. stainless steel pipe with 2-inch flanges welded to each end. The pipe also had 1/4 inch feed and effluent lines welded on 6 inches from the bottom and top of the reactor respectively. The top sealing flange was fitted with a pressure gauge and rupture disk. The bottom sealing flange had a thermocouple well welded directly in the center of the flange that extends up through the middle of the reactor pipe when attached. The thermocouple well was a 1/2 inch stainless steel tube welded shut at one end and contained eight or more thermocouple points. The reactor pipe was enclosed with a Lindberg three foot heating furnace containing three heating zones but only the bottom zone was used to preheat the butylene feed to the reaction section. The furnace was controlled by three controllers comprising a PID control block for monitoring and controlling the temperature inside the reactor at each zone. Located on the effluent line was tubing and equipment for the sampling system. The sampling system included an air actuated valve and a steam traced line of helium that carried the sample to the gas chromatograph (GC) for direct injection.

The product hood contained the effluent cooler, the condensables collection tank, and the effluent pressure transmitter. The effluent condenser consisted of a coiled tube that contained the effluent line as the inner tube. Cooling water flowed through the outer tube to cool the effluent containing inner tube. Downstream of the condenser was the 5 gallon condensables collection tank. The effluent pressure was controlled by a PID control block in the process control software. This control block consisted of a pressure transducer (located upstream of the condenser), an instrument to pneumatic signal converter, and a pressure control valve (located downstream of the collection tank). A vent for the noncondensables was located downstream of the pressure valve.

For the pentene isomerization examples, 1-pentene was pressurized with nitrogen in a 4-liter feed tank to about 60 psig and then fed to reactor consisting of a stainless steel tube with inside diameter of 1 inch. Flow to the reactor was controlled with a mass flow controller, positive-displacement flow meter and control valve. The outside of the reactor was heated with three Glas-Col heating mantles with corresponding temperature controllers. Feed was introduced into the top of the reactor through 1/4 inch feed lines with tubing connections.

A thermowell in the bottom of the reactor contained six thermocouples to measure temperature at various points in the reactor.

5 A refrigerated circulating bath with shell and tube heat exchanger was used to condense the vapors from the reactor at atmospheric pressure. During sample collection, liquid samples are collected in a cooled 1-liter stainless steel sample bomb and then analyzed on an external gas chromatograph with alumina plot column. Small amounts of gaseous product were vented through a small bubble meter used to monitor flow. Samples of this gaseous product were collected in gas sample bags, analyzed and included in the final product analysis.

10 The liquid reaction products were analyzed using a Sigma gas chromatograph through a J&W alumina-plot column utilizing a flame ionization detector. Gaseous samples were analyzed using a Hach gas chromatograph through a multi-column system utilizing both a thermal conductivity detector and flame ionization detector.

Testing Procedure

15 The reactor was first loaded with an inert packing material in the preheating zone. The inert packing materials used were either a small mesh corundum or inert clay catalyst support balls. The inert bed depth varied depending on the thermocouple points the catalyst was to occupy. A typical loading depth was about 30 inches of inert material. Above the packing material a weighed amount of catalyst is added to coincide with thermocouple points for reading temperature during the experiment. The amount of catalyst used for the test varied 20 depending on the weight hourly space velocity desired and the flow rates attainable with our equipment. A typical loading consisted of 97 grams of catalyst which corresponded to a loading of about 4 inches in the reactor. Above the catalyst another layer of packing material was added to form a distinct zone of catalyst.

25 Two different feed streams were used during the screening. One feed stream used was an MTBE processing effluent and comprised about 30-50% butene-2, 25-45% butene-1, and 20-30 % n-butane. The other feed stream used for testing comprised about 90% butene-2 and 9% butene-1 (termed herein "butylenes feed").

30 Testing began by warming up the reactor to a minimum operating temperature usually greater than 200°C. The warming step was performed under a nitrogen purge of approximately 15-50 psia. Once the reactor was warmed, the flow control valve was opened to introduce feed to the reactor, and the nitrogen purge was turned off. WHSVs varied from 1 to 30 during the testing. The operating temperatures used for the testing varied in a range from 200°C to 550°C and depended on many factors, including the activity of the catalyst. The pressures used during the testing varied in response to restriction from the catalyst and reactor. Most all of the testing was performed with the pressure control valve open to the atmosphere. The recorded values of the effluent pressure, however, were in a range of about 15-45 psia.

35 Samples of the reactor effluent were manually sampled using the sampling system and gas chromatography. Sampling was performed manually rather than on an automatic specific time interval in order to have specific operating conditions for the process variables. The analysis was performed with a boiling point separation column or an alumina column.

40 Many different techniques were attempted to regenerate the catalysts. One technique was to burn the "coke" off the catalyst by putting a weighed amount in the muffle furnace at about 500°C to 550°C for approximately 12 hours. In situ catalyst regeneration was also successful. Both methods restored catalyst activity.

The testing procedure for the n-pentene stream was essentially the same as for the n-butene stream, except that flow through the reactor was from the top down with the following additional differences:

1. The catalyst extrudate was diluted with alundum available from Norton.
2. Typical loadings included 3 inches of 5mm diameter glass beads at the bottom of the reactor. Next was loaded 3 inches of 3mm glass beads. A mixture containing catalyst extrudate diluted to 240cc with alundum was then loaded on top of the 3mm glass beads to a depth of 21 inches. Last was loaded 12 inches of alundum on top.
3. The catalyst was dried under flowing nitrogen at 400°C for 8 to 10 hours to remove moisture prior to introduction of pentene to the reactor.
- 50 4. During the experimental runs, the various reaction parameters such as temperatures, pressure and pentene feed rate were monitored and recorded by an Apple computer system with ISAAC interface.

Calculations

55 Conversion and selectivity are calculated for each sample during testing runs and used for comparison of the various catalysts. It is believed that during the isomerization an equilibrium is achieved between butene-1 and trans and cis butene-2. Therefore the calculation of conversion and selectivity reflect the feed (FD) and effluent (EFF) concentrations of butene-1 (B1) and butene-2 (B2) and isobutylene (IB1). Conversion is calcu-

lated as:

$$\% \text{ Conversion} = \frac{(\text{wt\% B1} + \text{wt\% B2})\text{FD} - (\text{wt\% B1} + \text{wt\% B2})\text{EFF}}{(\text{wt\% B1} + \text{wt\% B2})\text{FD}} \times 100$$

selectivity is calculated as:

$$5 \quad \% \text{ Selectivity} = \frac{(\text{wt\% IB1})\text{EFF} - (\text{wt\% IB1})\text{FD}}{(\text{wt\% B1} + \text{wt\% B2})\text{FD} - (\text{wt\% B1} + \text{wt\% B2})\text{EFF}} \times 100$$

and yield is calculated as

$$10 \quad \% \text{ Yield} = \frac{(\text{wt\% IB1}) \text{ EFF} - (\text{wt\% IB1}) \text{ FD}}{(\text{wt\% B1} + \text{wt\% B2}) \text{ FD}} \times 100$$

EXAMPLE 1

CATALYST: H-FERRIERITE NO. 1

CATALYST CHARGE: 400 grams

15 PRESSURE : 15-17 psia

WHSV: 2

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CONDITIONS & COMPONENTS	FEED wt %	EFF @ 1 HR	EFF @ 5.6 HRS	EFF @ 16 HRS	EFF @ 36 HRS
INLET TEMPERATURE		370°C	295°C	255°C	319°C
METHANE	0.00	0.08	0.00	0.00	0.00
ETHANE	0.01	0.13	0.01	0.01	0.01
ETHYLENE	1.17	0.20	0.17	0.33	0.25
PROPANE	0.00	3.14	0.08	0.03	0.10
CYCLO PROPANE	0.00	0.00	0.00	0.00	0.00
PROPYLENE	0.15	2.02	0.69	0.52	0.95
ISO-BUTANE	0.01	1.18	0.17	0.06	0.17
N-BUTANE	0.09	4.97	1.50	1.11	1.54
METHYL CYC-PROPANE	0.00	0.00	0.00	0.00	0.00
TRANS 2-BUTENE	57.67	3.46	10.95	20.17	10.43
BUTENE-1	11.37	1.45	3.56	7.84	4.52
ISOBUTYLENE	0.02	7.69	16.10	12.57	19.50
CIS 2-BUTENE	29.45	2.38	7.45	14.21	7.17
1,3 BUTADIENE	0.01	0.00	0.00	0.00	0.00
HEAVIES (C5+)	0.05	73.30	59.32	43.15	55.36

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EXAMPLE 2

CATALYST: H-FERRIERITE NO. 1

CATALYST CHARGE: 400 grams

PRESSURE: 15-17 psia

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	CONDITIONS & COMPONENTS	FEED wt %	EFF @ 9 HRS	EFF @ 21 HRS	EFF @ 31 HRS	EFF @ 49 HRS
10	INLET TEMPERATURE WHSV		295°C 3	350°C 8	274°C 4	161°C 15
	METHANE	0.00	0.00	0.01	0.00	0.07
	ETHANE	0.01	0.01	0.02	0.01	0.12
15	ETHYLENE	1.17	0.22	0.28	0.46	0.84
	PROPANE	0.00	0.07	0.15	0.03	0.64
	CYCLO PROPANE	0.00	0.00	0.00	0.00	0.00
20	PROPYLENE	0.15	0.69	1.31	0.41	3.66
	ISO-BUTANE	0.01	0.13	0.17	0.07	0.55
	N-BUTANE	0.09	1.24	1.42	0.97	3.08
	CH ₃ CYC-PROPANE	0.00	0.00	0.00	0.00	0.00
25	TRANS 2-BUTENE	57.67	12.49	9.74	23.13	18.58
	BUTENE-1	11.37	4.43	4.13	8.86	10.21
	ISOBUTYLENE	0.02	14.83	17.94	11.29	26.95
30	CIS 2-BUTENE	29.45	8.65	6.89	15.72	13.69
	1,3 BUTADIENE	0.01	0.00	0.00	0.00	0.05
	HEAVIES (CS+)	0.05	57.24	57.94	39.05	21.56

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EXAMPLE 3

CATALYST: H-FERREIRITE NO. 1
 CATALYST CHARGE: 96 grams
 PRESSURE: 15-17 psia
 WHSV: 15

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	CONDITIONS & COMPONENTS	FEED wt %	EFF @ 2 HRS	EFF @ 12 HRS	EFF @ 24 HRS	EFF @ 31 HRS	EFF @ 39 HRS
5	INLET TEMPERATURE		251°C	319°C	371°C	372°C	371°C
10	METHANE	0.00	0.00	0.01	0.00	0.00	0.00
15	ETHANE	0.01	0.01	0.02	0.01	0.01	0.01
20	ETHYLENE	1.17	0.60	0.72	0.55	0.80	0.84
25	PROPANE	0.00	0.04	0.09	0.03	0.02	0.01
30	CYCLO PROPANE	0.00	0.00	0.00	0.00	0.00	0.00
35	PROPYLENE	0.15	0.19	1.25	0.81	0.70	0.57
40	ISO-BUTANE	0.01	0.02	0.12	0.06	0.03	0.02
45	N-BUTANE	0.09	0.47	1.22	0.86	0.72	0.55
50	METHYL CYC- PROPANE	0.00	0.00	0.00	0.01	0.04	0.02
55	TRANS 2-BUTENE	57.67	40.93	20.76	26.05	28.33	32.28
60	BUTENE-1	11.37	17.60	9.59	13.95	14.14	16.47
65	ISOBUTYLENE	0.02	2.65	23.53	31.89	26.97	21.72
70	CIS 2-BUTENE	29.45	26.20	14.67	18.23	20.15	23.48
75	1,3 BUTADIENE	0.01	0.00	0.00	0.00	0.00	0.00
80	HEAVIES (C5+)	0.05	11.29	28.02	7.55	8.09	4.03

35 EXAMPLE 4

The operating conditions for the next experimental run are as follows:

CATALYST: H-Ferrierite No. 1
40 FEED: Butylenes
CATALYST WT.: 97 grams
RUNTIME HOURS: 180 hrs.
INLET TEMPS.: 310°-420°C
WHSV: 15
45 PRESSURE: 18 psia avg.
CONVERSION: 26.6%
SELECTIVITY: 70.1%

For this experimental run, 97.7 grams of fresh catalyst was loaded in the reactor. During this experimental run hydrogen gas was added to the feed via the auxiliary feed line for 8-20 hours periodically over the 180 hour run time. The hydrogen was added to the feed in an attempt to decrease "coking". The gasoline went from pale green to near water white in appearance in contrast to the pale green gasoline produced in runs without hydrogen.

55 EXAMPLE 5

For this experiment, a sample of "coked" hydrogen ferrierite No. 1 was placed in the muffle furnace for about 12 hours at 500°C in order to regenerate the catalyst by burning off the "coke". The catalyst returned from the regeneration with a white color similar to the original material. The catalyst sample was loaded into

the reactor and charged with a butylene stream.

CATALYST: H-FERRIERITE NO. 1 (REGENERATED)

CATALYST CHARGE 97.70 grams

PRESSURE : 17-24 psia

5 WHSV: 15

10	CONDITIONS & COMPONENTS	FEED wt %	EFF @ 2 HRS wt %	EFF @ 12 HRS wt %	EFF @ 24 HRS wt %	EFF @ 48 HRS wt %	EFF @ 67 HRS wt %
15	INLET TEMPERATURE (C)		390°C	402°C	398°C	405°C	400°C
15	METHANE	0.00	0.02	0.01	0.00	0.03	0.00
15	ETHANE	0.01	0.04	0.01	0.01	0.00	0.01
15	ETHYLENE	0.86	0.07	0.63	0.67	0.02	0.87
20	PROPANE	0.00	0.00	0.00	0.00	0.01	0.01
20	CYCLO PROPANE	0.00	0.00	0.00	0.00	0.00	0.00
20	PROPYLENE	0.12	2.67	1.21	0.77	0.36	0.54
20	ISO-BUTANE	0.00	0.25	0.08	0.05	0.02	0.06
25	N-BUTANE	0.04	1.91	1.07	0.79	0.48	0.82
25	METHYL CYC-PROPANE	0.00	0.00	0.00	0.00	0.00	0.00
25	TRANS 2-BUTENE	57.88	18.75	24.12	27.83	32.56	36.09
30	BUTENE-1	10.74	9.70	12.72	13.89	18.68	21.07
30	ISOBUTYLENE	0.00	34.14	34.70	30.62	21.05	12.73
30	CIS 2-BUTENE	30.26	13.78	17.46	20.02	23.84	25.99
35	1,3 BUTADIENE	0.01	0.00	0.00	0.00	0.00	0.00
35	HEAVIES (C5+)	0.08	18.68	7.99	5.34	2.95	1.81

40 The following Examples 6-26 feature data illustrating isobutylene conversion using an MTBE processing effluent feed. The testing apparatus and procedure were the same as described above.

EXAMPLE 6

45 CATALYST: H-FERRIERITE NO. 1
 CATALYST CHARGE: 97.70 grams
 PRESSURE : 17-18 psia
 INLET ET TEMPERATURE : 390°C
 50 WHSV: 14

	COMPONENTS	INITIAL FEED wt %	INITIAL EFF wt %	FEED @ 12 HRS wt %	EFF @ 12 HRS wt %	FEED @ 24 HRS wt %	EFF @ 24 HRS wt %	FEED @ 48 HRS wt %	EFF @ 48 HRS wt %
5	METHANE	0.08	0.06	0.08	0.05	0.01	0.01	0.01	0.00
10	ETHANE	0.00	0.02	0.00	0.00	0.00	0.00	0.00	0.00
	ETHYLENE	0.00	0.05	0.00	0.01	0.00	0.01	0.00	0.00
	PROPANE	0.00	0.06	0.00	0.00	0.00	0.00	0.00	0.00
15	CYCLO PROPANE	0.00	0.00	0.00	0.00	0.00	0.01	0.00	0.01
	PROPYLENE	0.00	0.77	0.00	0.33	0.00	0.26	0.00	0.15
	ISO-BUTANE	2.89	2.75	2.90	2.80	3.15	3.04	3.14	3.02
	N-BUTANE	25.98	25.49	25.99	26.20	19.95	20.11	19.88	20.05
20	METHYL CYC-PROPANE	0.06	0.16	0.05	0.16	0.07	0.17	0.07	0.17
	TRANS 2-BUTENE	24.38	18.16	24.39	21.54	16.54	25.00	16.46	28.09
25	BUTENE-1	28.31	9.90	28.29	12.01	49.00	14.41	49.19	16.10
	ISOBUTY-LENE	0.24	20.66	0.23	17.64	0.26	15.77	0.25	10.61
	CIS 2-BUT-ENE	17.90	13.12	17.88	15.32	10.78	18.16	10.74	20.40
30	1,3 BUTA-DIENE	0.00	0.01	0.00	0.01	0.07	0.01	0.08	0.01
	HEAVIES (C5+)	0.17	8.80	0.17	3.94	0.18	3.04	0.17	1.39

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40 EXAMPLE 7

CATALYST: H-FERRIERITE NO. 1
 CATALYST CHARGE: 97.70 grams
 PRESSURE: 17 psia
 45 INLET TEMPERATURE: 400°C
 WHSV: 14

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	COMPONENTS	INITIAL FEED wt %	INITIAL EFF wt %	FEED @ 12 HRS wt %	EFF @ 12 HRS wt %	FEED @ 24 HRS wt %	EFF @ 24 HRS wt %	FEED @ 48 HRS wt %	EFF @ 48 HRS wt %
5	METHANE	0.00	0.07	0.00	0.01	0.01	0.02	0.01	0.01
10	ETHANE	0.00	0.05	0.00	0.00	0.00	0.00	0.00	0.00
15	ETHYLENE	0.01	0.26	0.01	0.02	0.00	0.01	0.00	0.00
20	PROPANE	0.00	0.27	0.00	0.02	0.00	0.01	0.00	0.00
25	CYCLO PROPANE	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
30	PROPYLENE	0.00	2.51	0.00	0.53	0.00	0.48	0.00	0.27
35	ISO-BUTANE	3.41	3.84	3.41	2.77	3.49	3.34	3.38	3.31
40	N-BUTANE	21.81	23.88	21.81	20.55	22.00	22.45	22.15	22.52
45	METHYL CYC-PROPANE	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
50	TRANS 2-BUTENE	17.68	15.47	17.68	18.08	17.47	22.66	17.24	26.06
55	BUTENE-1	43.69	7.56	43.69	8.43	43.87	10.45	43.83	12.12
60	ISOBUTY-LENE	0.41	27.92	0.41	20.21	0.35	20.23	0.44	14.95
65	CIS 2-BUTENE	12.67	10.84	12.67	12.92	12.51	15.93	12.67	18.22
70	1,3 BUTADI-ENE	0.02	0.00	0.02	0.00	0.01	0.00	0.02	0.00
75	HEAVIES (CS+)	0.29	7.31	0.29	17.39	0.29	4.42	0.27	2.54

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EXAMPLE 8

45 CATALYST: H-FERRIERITE NO. 1
 CATALYST CHARGE: 97.70 grams
 PRESSURE: 17-22 psia
 INLET TEMPERATURE: 410°C
 WHSV: 14

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	COMPONENTS	INITIAL FEED wt %	INITIAL EFF wt %	FEED @ 12 HRS wt %	EFF @ 12 HRS wt %	FEED @ 24 HRS wt %	EFF @ 24 HRS wt %	FEED @ 48 HRS wt %	EFF @ 48 HRS wt %
	METHANE	0.11	0.08	0.08	0.05	0.08	0.02	0.05	0.02
10	ETHANE	0.00	0.01	0.00	0.00	0.00	0.00	0.00	0.00
	ETHYLENE	0.00	0.04	0.00	0.02	0.00	0.01	0.00	0.01
15	PROPANE	0.00	0.03	0.00	0.01	0.00	0.00	0.00	0.00
	CYCLO PROPANE	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
	PROPYLENE	0.00	0.82	0.00	0.46	0.00	0.26	0.00	0.18
20	ISO-BUTANE	3.24	3.25	3.47	3.42	3.50	3.35	3.29	3.21
	N-BUTANE	29.63	30.09	23.69	24.46	23.71	24.25	22.97	23.40
	METHYL CYC-PROPANE	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
25	TRANS 2-BUTENE	27.38	16.59	22.30	20.70	22.29	23.27	23.57	25.12
	BUTENE-1	19.39	9.53	33.49	12.06	33.46	13.56	30.83	13.58
	ISOBUTY-LENE	0.19	21.81	0.27	21.20	0.27	16.72	0.36	15.16
30	CIS 2-BUT-ENE	19.84	12.12	16.48	15.10	16.50	16.98	18.73	17.98
	1,3 BUTADIENE	0.00	0.01	0.00	0.01	0.00	0.01	0.00	0.01
35	HEAVIES (C5+)	0.22	5.62	0.22	2.51	0.20	1.57	0.22	1.35

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EXAMPLE 9

45 CATALYST: H-FERRIERITE NO. 1
 CATALYST CHARGE: 97.70 grams
 PRESSURE: 24-25 psia
 INLET TEMPERATURE: 425°C
 WHSV: 14

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	COMPONENTS	INITIAL FEED wt %	INITIAL EFF wt %	FEED @ 12 HRS wt %	EFF @ 12 HRS wt %	FEED @ 24 HRS wt %	EFF @ 24 HRS wt %	FEED @ 48 HRS wt %	EFF @ 48 HRS wt %
	METHANE	0.02	0.04	0.00	0.03	0.02	0.02	0.03	0.02
10	ETHANE	0.00	0.01	0.00	0.00	0.00	0.00	0.00	0.00
	ETHYLENE	0.00	0.04	0.00	0.02	0.00	0.00	0.00	0.00
15	PROPANE	0.00	0.02	0.00	0.00	0.00	0.00	0.00	0.00
	CYCLO PROPANE	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
	PROPYLENE	0.00	0.68	0.00	0.29	0.00	0.10	0.00	0.04
20	ISO-BUTANE	3.11	3.28	3.02	3.19	3.24	3.14	3.24	3.09
	N-BUTANE	23.09	23.63	23.17	23.37	22.95	23.01	20.35	20.34
25	METHYL CYC- PROPANE	0.07	0.01	0.07	0.01	0.06	0.01	0.07	0.01
	TRANS 2- BUTENE	19.81	18.93	20.10	22.42	19.58	26.76	16.43	30.10
	BUTENE-1	38.65	11.80	38.12	14.04	39.25	16.81	48.28	19.22
	ISOBUTYLEN E	0.23	24.14	0.25	18.21	0.22	9.38	0.34	4.25
30	CIS 2- BUTENE	14.84	14.15	15.06	16.70	14.49	20.01	11.02	22.64
	1,3 BUTADIENE	0.00	0.01	0.01	0.01	0.00	0.01	0.05	0.02
35	HEAVIES (C5+)	0.19	3.09	0.20	1.54	0.18	.56	0.18	.09

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EXAMPLE 10

45 CATALYST: H-FERRIERITE NO. 1
 CATALYST CHARGE: 97.70 grams
 PRESSURE: 17-25 psia
 FEED: MTBE processing effluent

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ISOBUTYLENE YIELD

(grams isobutylene formed per grams normal butenes in feed)

	REACTOR INLET TEMP	WHS V	INITIAL	@ 12 HRS	@ 24 HRS	@ 48 HRS	@ 72 HRS	@ 84 HRS	@ 96 HRS	@ 120 HRS
5	390°C	14	29.17	24.91	20.60	13.84				
10	400°C	14	37.50	29.10	27.26	20.16				
	410°C	14	26.25	27.97	23.06	20.63				
	425°C	14	32.83	24.77	12.76	5.59				
15	400°C	7	18.37*	14.73	11.51	8.89				
	425°C	7	30.87**	28.76	23.36	19.04	16.69	16.03	14.64	12.81
	440°C	7	35.77	33.79	29.42	19.78	13.35	11.03		

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% SELECTIVITY

(grams isobutylene formed per grams normal butenes consumed)

	REACTOR INLET TEMP	WHS V	INITIAL	@ 12 HRS	@ 24 HRS	@ 48 HRS	@ 72 HRS	@ 84 HRS	@ 96 HRS	@ 120 HRS
25	390°C	14	69.46	80.23	82.79	87.75				
	400°C	14	68.48	61.89	80.12	83.74				
	410°C	14	76.20	86.83	89.34	89.37				
	425°C	14	84.13	89.24	94.16	103.76				
35	400°C	7	52.46*	66.10	70.88	66.12				
	425°C	7	72.64**	85.97	86.95	90.19	89.05	90.46	96.86	95.00
	440°C	7	71.47	91.61	95.06	97.86	99.00	99.83		

40 * 1.7 HOURS

** 2.47 HOURS

EXAMPLE 11

45 CATALYST: H-FERRIERITE NO. 1
 CATALYST CHARGE: 97.88 grams
 PRESSURE: 17-18 psia
 INLET TEMPERATURE: 425°C
 50 WHSV: 7

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	COMPONENTS	FEED @ 2.5 HRS wt %	EFF @ 2.5 HRS wt %	FEED @ 12 HRS wt %	EFF @ 12 HRS wt %	FEED @ 24 HRS wt %	EFF @ 24 HRS wt %	FEED @ 48 HRS wt %	EFF @ 48 HRS wt %
5	METHANE	0.07	0.05	0.07	0.03	0.03	0.03	0.05	0.01
10	ETHANE	0.00	0.01	0.00	0.02	0.00	0.01	0.00	0.01
	ETHYLENE	0.00	0.04	0.00	0.00	0.00	0.00	0.00	0.00
15	PROPANE	0.00	0.04	0.00	0.01	0.00	0.00	0.00	0.00
	CYCLO PROPANE	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
20	PROPYLENE	0.00	0.75	0.00	0.34	0.00	0.23	0.00	0.16
	ISO-BUTANE	2.99	2.87	2.99	2.91	2.94	2.92	3.11	3.00
25	N-BUTANE	21.43	21.42	21.43	21.89	21.46	21.80	22.06	22.39
	METHYL CYC- PROPANE	0.06	0.00	0.06	0.00	0.06	0.00	0.07	0.00
30	TRANS 2- BUTENE	24.41	19.71	24.41	22.78	24.55	25.15	25.14	26.92
	BUTENE-1	32.61	9.53	32.61	11.09	32.31	12.07	30.25	12.88
	ISOBUTYLE NE	0.33	23.47	0.33	21.89	0.35	17.87	0.25	14.40
35	CIS 2- BUTENE	17.94	13.86	17.94	16.01	18.13	17.62	19.00	18.80
	1,3 BUTADIENE	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
	HEAVIES (C5+)	0.16	8.25	0.16	3.03	0.17	2.30	0.07	1.44

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EXAMPLE 11 (Continued)

	COMPONENTS	FEED @ 72 HRS wt %	EFF @ 72 HRS wt %	FEED @ 96 HRS wt %	EFF @ 96 HRS wt %	FEED @ 120 HRS wt %	EFF @ 120 HRS wt %
5	METHANE	0.02	0.01	0.02	0.00	0.02	0.01
10	ETHANE	0.00	0.00	0.00	0.00	0.00	0.00
15	ETHYLENE	0.00	0.00	0.00	0.00	0.00	0.00
20	PROPANE	0.00	0.00	0.00	0.00	0.00	0.00
25	CYCLO PROPANE	0.00	0.00	0.00	0.00	0.00	0.00
30	PROPYLENE	0.00	0.14	0.00	0.11	0.00	0.10
35	ISO-BUTANE	3.29	3.19	3.26	3.21	3.27	3.18
40	N-BUTANE	18.36	18.71	18.56	18.99	18.59	18.85
45	METHYL CYC- PROPANE	0.07	0.00	0.07	0.00	0.07	0.00
50	TRANS 2- BUTENE	18.19	29.04	18.48	30.37	18.68	30.74
55	BUTENE-1	47.41	13.95	46.61	14.58	46.34	14.86
60	ISOBUTYLENE	0.24	13.24	0.25	11.62	0.24	10.19
65	CIS 2-BUTENE	12.28	20.30	12.60	21.01	12.63	21.59
70	1,3 BUTADIENE	0.00	0.00	0.01	0.00	0.01	0.01
75	HEAVIES (C5+)	0.14	1.41	0.14	0.11	0.15	0.47

EXAMPLE 12

CATALYST: H-FERRIERITE NO. 1
 CATALYST CHARGE: 97.70 grams
 PRESSURE: 16 psia
 40 INLET TEMPERATURE: 440°C
 WHSV: 7

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	COMPONENTS	FEED @ INITIAL wt %	EFF @ INITIAL wt %	FEED @ 12 HRS wt %	EFF @ 12 HRS wt %	FEED @ 24 HRS wt %	EFF @ 24 HRS wt %
5	METHANE	0.07	0.08	0.07	0.04	0.10	0.05
10	ETHANE	0.00	0.04	0.00	0.01	0.00	0.00
15	ETHYLENE	0.00	0.26	0.00	0.04	0.00	0.03
20	PROPANE	0.00	0.17	0.00	0.00	0.00	0.00
25	CYCLO PROPANE	0.00	0.00	0.00	0.00	0.00	0.00
30	PROPYLENE	0.00	1.66	0.00	0.36	0.00	0.23
	ISO-BUTANE	3.44	3.29	3.44	3.38	3.39	3.26
	N-BUTANE	20.73	20.94	20.73	20.96	21.02	21.25
	METHYL CYC- PROPANE	0.06	0.00	0.06	0.00	0.06	0.00
	TRANS 2- BUTENE	21.76	16.22	21.76	19.86	22.82	21.71
	BUTENE-1	37.78	9.50	37.78	12.85	35.21	13.94
	ISOBUTYLENE	0.25	27.20	0.25	25.70	0.25	22.34
	CIS 2-BUTENE	15.80	11.92	15.80	14.84	17.04	16.18
	1,3 BUTADIENE	0.00	0.01	0.00	0.02	0.00	0.02
	HEAVIES (C5+)	0.11	8.71	0.11	1.94	0.11	0.99

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EXAMPLE 12 (Continued)

	COMPONENTS	FEED @ 48 HRS wt %	EFF @ 48 HRS wt %	FEED @ 72 HRS wt %	EFF @ 72 HRS wt %	FEED @ 92 HRS wt %	EFF @ 92 HRS wt %
	METHANE	0.06	0.01	0.02	0.02	0.08	0.06
10	ETHANE	0.00	0.00	0.00	0.00	0.01	0.01
	ETHYLENE	0.00	0.02	0.00	0.01	0.00	0.01
15	PROPANE	0.00	0.00	0.00	0.00	0.00	0.00
	CYCLO PROPANE	0.00	0.00	0.00	0.00	0.00	0.00
	PROPYLENE	0.00	0.12	0.00	0.07	0.00	0.04
20	ISO-BUTANE	3.37	3.21	3.43	3.29	3.33	3.22
	N-BUTANE	20.71	20.87	20.13	20.22	22.14	22.18
	METHYL CYC- PROPANE	0.07	0.00	0.07	0.00	0.07	0.00
25	TRANS 2- BUTENE	22.29	25.18	20.13	27.47	17.63	27.38
	BUTENE-1	36.62	16.22	41.86	17.79	42.58	18.34
	ISOBUTYLENE	0.25	15.17	0.25	10.40	0.44	7.83
30	CIS 2-BUTENE	16.52	18.78	14.01	20.48	13.51	20.60
	1,3 BUTADIENE	0.00	0.04	0.00	0.06	0.00	0.07
	HEAVIES (C5+)	0.11	0.38	0.10	0.19	0.21	0.26

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FIG. 1 is a graph of the conversion and selectivity wt% versus run time depicting the results of this example.
 FIG. 2 is a graph of isobutylene yield and isobutylene wt% versus run time for the results of this example.

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EXAMPLE 13

CATALYST: H-FERRIERITE NO. 1
 CATALYST CHARGE: 160.00 grams
 45 PRESSURE: 14.9 - 15.3 psia
 INLET TEMPERATURE: 340°C
 WHSV: 4.5

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	COMPONENTS	FEED @ 3.7 HRS wt %	EFF @ 3.7 HRS wt %	FEED @ 12 HRS wt %	EFF @ 12 HRS wt %	FEED @ 24 HRS wt %	EFF @ 24 HRS wt %
5	METHANE	0.01	0.01	0.01	0.00	0.01	0.01
10	ETHANE	0.00	0.01	0.00	0.00	0.00	0.00
15	ETHYLENE	0.00	0.06	0.00	0.02	0.00	0.01
20	PROPANE	0.00	0.14	0.00	0.03	0.00	0.02
25	CYCLO PROPANE	0.00	0.00	0.00	0.00	0.00	0.00
30	PROPYLENE	0.00	1.38	0.00	0.70	0.00	0.53
	ISO-BUTANE	3.18	3.12	3.18	2.61	3.18	2.65
	N-BUTANE	23.04	23.6943	23.04	20.90	23.04	20.88
	METHYL CYC- PROPANE	0.08	0.00	0.08	0.00	0.08	0.00
	TRANS 2- BUTENE	19.59	15.27	19.59	14.93	19.59	16.68
	BUTENE-1	39.77	7.66	39.77	7.80	39.77	8.38
	ISOBUTYLENE	0.78	24.60	0.78	21.89	0.78	20.47
	CIS 2-BUTENE	13.29	10.81	13.29	10.95	13.29	11.92
	1,3 BUTADIENE	0.01	0.00	0.01	0.00	0.01	0.00
	HEAVIES (C5+)	0.00	12.99	0.00	19.92	0.00	18.21

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EXAMPLE 13 (Continued)

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	COMPONENTS	FEED @ 36 HRS wt %	EFF @ 36 HRS wt %	FEED @ 48 HRS wt %	EFF @ 48 HRS wt %	FEED @ 70 HRS wt %	EFF @ 70 HRS wt %
10	METHANE	0.01	0.00	0.01	0.00	0.01	0.00
	ETHANE	0.00	0.00	0.00	0.00	0.00	0.00
	ETHYLENE	0.00	0.01	0.00	0.01	0.00	0.01
15	PROPANE	0.00	0.01	0.00	0.01	0.00	0.01
	CYCLO PROPANE	0.00	0.00	0.00	0.00	0.00	0.00
	PROPYLENE	0.00	0.43	0.00	0.37	0.00	0.28
20	ISO-BUTANE	3.18	2.69	3.18	2.74	3.18	2.88
	N-BUTANE	23.04	21.30	23.04	21.90	23.04	22.38
	METHYL CYC- PROPANE	0.08	0.01	0.08	0.00	0.08	0.01
25	TRANS 2- BUTENE	19.59	18.56	19.59	20.11	19.59	23.18
	BUTENE-1	39.77	9.35	39.77	10.16	39.77	11.31
	ISOBUTYLENE	0.78	19.05	0.78	18.20	0.78	15.30
30	CIS 2-BUTENE	13.29	13.26	13.29	14.35	13.29	16.34
	1,3 BUTADIENE	0.01	0.00	0.01	0.00	0.01	0.00
	HEAVIES (CS+)	0.00	15.10	0.00	11.89	0.00	8.05

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FIG. 3 is a graph of the conversion and selectivity wt% versus run time depicting the results of this example.
 FIG. 4 is a graph of isobutylene yield and isobutylene wt% versus run time for the results of this example.

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EXAMPLE 14

CATALYST: H-FERRIERITE NO. 1
 CATALYST CHARGE: 400.33 grams
 45 PRESSURE: 14.7 - 15.3 psia
 INLET TEMPERATURE : 370°C
 WHSV: 1.8

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	COMPONENTS	FEED @ 5 HRS wt %	EFF @ 5 HRS wt %	FEED @ 25 HRS wt %	EFF @ 25 HRS wt %	FEED @ 50 HRS wt %	EFF @ 50 HRS wt %
5	METHANE	0.01	0.02	0.01	0.01	0.01	0.01
	ETHANE	0.00	0.03	0.00	0.01	0.00	0.00
	ETHYLENE	0.00	0.15	0.00	0.04	0.00	0.02
10	PROPANE	0.00	0.33	0.00	0.07	0.00	0.04
	CYCLO PROPANE	0.00	0.00	0.00	0.00	0.00	0.00
	PROPYLENE	0.00	2.42	0.00	1.06	0.00	0.80
15	ISO-BUTANE	3.21	3.54	3.21	2.65	3.21	2.60
	N-BUTANE	23.01	25.82	23.01	20.02	23.01	20.10
	METHYL CYC- PROPANE	0.08	0.00	0.08	0.00	0.08	0.00
20	TRANS 2- BUTENE	19.55	12.57	19.55	11.77	19.55	12.58
	BUTENE-1	39.84	6.00	39.84	5.47	39.84	6.07
25	39.84 ISOBUTYLE NE	0.79	26.4	0.79	23.45	0.79	24.39
	CIS 2-BUTENE	13.25	8.74	13.25	8.26	13.25	9.06
	1,3 BUTADIENE	0.01	0.00	0.01	0.00	0.01	0.00
30	HEAVIES (C5+)	0.00	13.69	0.00	26.98	0.00	24.11

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EXAMPLE 14 (Continued)

	COMPONENTS	FEED @ 75 HRS wt %	EFF @ 75 HRS wt %	FEED @ 100 HRS wt %	EFF @ 100 HRS wt %	FEED @ 147 HRS wt %	EFF @ 147 HRS wt %
5	METHANE	0.01	0.00	0.01	0.00	0.01	0.00
10	ETHANE	0.00	0.00	0.00	0.00	0.00	0.00
	ETHYLENE	0.00	0.02	0.00	0.01	0.00	0.00
15	PROPANE	0.00	0.02	0.01	0.00	0.00	0.01
	CYCLO PROPANE	0.00	0.00	0.00	0.00	0.00	0.00
	PROPYLENE	0.00	0.60	0.00	0.48	0.00	0.36
20	ISO-BUTANE	3.21	2.63	3.21	2.71	3.21	2.96
	N-BUTANE	23.01	20.61	23.01	21.18	23.01	23.08
25	METHYL CYC- PROPANE	0.08	0.00	0.08	0.00	0.08	0.00
	TRANS 2- BUTENE	19.55	14.05	19.55	15.75	19.55	19.71
	BUTENE-1	39.84	6.76	39.84	7.53	39.84	9.43
	ISOBUTYLENE	0.79	24.96	0.79	24.69	0.79	23.69
30	CIS 2-BUTENE	13.25	10.05	13.25	11.19	13.25	13.93
	1,3 BUTADIENE	0.01	0.00	0.01	0.00	0.01	0.00
	HEAVIES (C5+)	0.00	20.07	0.00	16.21	0.00	6.56

35 EXAMPLE 15

CATALYST: H-FERRIERITE NO. 1
 CATALYST CHARGE: 400.06 grams
 PRESSURE: 14.7 - 15.3 psia
 40 INLET TEMPERATURE: 400°C
 WHSV: 1.8

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	COMPONENTS	FEED @ INITIAL wt %	EFF @ INITIAL wt %	FEED @ 12 HRS wt %	EFF @ 12 HRS wt %	FEED @ 24 HRS wt %	EFF @ 24 HRS wt %
5	METHANE	0.01	0.02	0.01	0.01	0.01	0.00
10	ETHANE	0.00	0.03	0.00	0.01	0.00	0.00
15	ETHYLENE	0.00	0.13	0.00	0.05	0.00	0.01
20	PROPANE	0.00	0.20	0.00	0.05	0.00	0.01
25	CYCLO PROPANE	0.00	0.00	0.00	0.00	0.00	0.00
30	PROPYLENE	0.00	1.72	0.00	1.03	0.00	0.39
	ISO-BUTANE	3.19	2.47	3.19	2.61	3.19	3.05
	N-BUTANE	23.06	18.33	23.06	19.82	23.06	23.10
	METHYL CYC- PROPANE	0.08	0.00	0.08	0.00	0.08	0.00
	TRANS 2- BUTENE	19.59	9.76	19.59	12.2	19.59	21.33
	BUTENE-1	39.71	4.99	39.71	6.30	39.71	7.62
	ISOBUTYLENE	0.78	19.12	0.78	23.98	0.78	20.56
	CIS 2-BUTENE	13.32	7.07	13.32	8.71	13.32	13.76
	1,3 BUTADIENE	0.01	0.00	0.01	0.00	0.01	0.00
	HEAVIES (C5+)	0.00	35.93	0.00	25.00	0.00	9.90

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EXAMPLE 15 (Continued)

	COMPONENTS	FEED @ 48 HRS wt %	EFF @ 48 HRS wt %	FEED @ 72 HRS wt %	EFF @ 72 HRS wt %	FEED @ 92 HRS wt %	EFF @ 92 HRS wt %
5	METHANE	0.01	0.01	0.01	0.01	0.01	0.07
10	ETHANE	0.00	0.01	0.00	0.00	0.00	0.00
	ETHYLENE	0.00	0.02	0.00	0.01	0.00	0.01
	PROPANE	0.00	0.02	0.00	0.01	0.00	0.02
15	CYCLO PROPANE	0.00	0.00	0.00	0.00	0.00	0.00
	PROPYLENE	0.00	0.60	0.00	0.34	0.00	0.20
	ISO-BUTANE	3.19	2.95	3.19	2.84	3.19	2.98
20	N-BUTANE	23.06	22.29	23.06	22.67	23.06	22.82
	METHYL CYC- PROPANE	0.08	0.00	0.08	0.01	0.08	0.01
25	TRANS 2- BUTENE	19.59	15.49	19.59	18.51	19.59	21.88
	BUTENE-1	39.71	7.76	39.71	9.80	39.71	11.24
	ISOBUTYLENE	0.78	27.99	0.78	25.08	0.78	20.39
30	CIS 2-BUTENE	13.32	10.93	13.32	13.22	13.32	15.51
	1,3 BUTADIENE	0.01	0.00	0.01	0.01	0.01	0.01
	HEAVIES (C5+)	0.00	11.69	0.00	7.24	0.00	4.70

35 EXAMPLE 15

CATALYST: H-FERRIERITE NO. 2
 CATALYST CHARGE: 97.75 grams
 PRESSURE: 18.7 psia
 40 INLET TEMPERATURE: 430°C
 WHSV: 7

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	COMPONENTS	FEED @ 2.4 HRS wt %	EFF @ 2.4 HRS wt %	FEED @ 12 HRS wt %	EFF @ 12 HRS wt %	FEED @ 24 HRS wt %	EFF @ 24 HRS wt %
5	METHANE	0.02	0.03	0.02	0.02	0.01	0.02
	ETHANE	0.00	0.03	0.00	0.01	0.00	0.01
10	ETHYLENE	0.00	0.21	0.00	0.09	0.00	0.07
	PROPANE	0.00	0.11	0.00	0.03	0.00	0.02
15	CYCLO PROPANE	0.00	0.00	0.00	0.00	0.00	0.00
	PROPYLENE	0.00	1.79	0.33	1.04	0.00	0.80
20	ISO-BUTANE	2.91	2.73	2.91	2.80	2.90	2.81
	N-BUTANE	27.81	27.04	27.81	28.10	27.82	28.27
25	METHYL CYC- PROPANE	0.07	0.01	0.07	0.01	0.07	0.00
	TRANS 2- BUTENE	21.51	11.35	21.51	14.62	21.50	15.13
30	BUTENE-1	31.37	7.67	31.37	8.58	31.36	8.83
	ISOBUTYLENE	0.50	24.86	0.50	27.55	0.49	28.24
35	CIS 2-BUTENE	15.62	9.55	15.62	10.59	15.65	10.23
	1,3 BUTADIENE	0.00	0.01	0.00	0.01	0.00	0.00
40	HEAVIES (C5+)	0.01	12.58	0.01	6.35	0.00	4.67

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EXAMPLE 15 (Continued)

	COMPONENTS	FEED @ 48 HRS wt %	EFF @ 48 HRS wt %	FEED @ 72 HRS wt %	EFF @ 72 HRS wt %	FEED @ 96 HRS wt %	EFF @ 96 HRS wt %
5	METHANE	0.00	0.01	0.01	0.01	0.01	0.01
10	ETHANE	0.00	0.01	0.00	0.01	0.00	0.01
	ETHYLENE	0.01	0.05	0.00	0.04	0.00	0.04
	PROPANE	0.00	0.01	0.00	0.01	0.00	0.01
15	CYCLO PROPANE	0.00	0.00	0.00	0.00	0.00	0.00
	PROPYLENE	0.00	0.61	0.00	0.51	0.00	0.44
	ISO-BUTANE	2.89	2.78	2.90	2.80	2.82	2.72
20	N-BUTANE	27.86	28.34	27.87	28.41	27.91	28.50
	METHYL CYC- PROPANE	0.07	0.01	0.08	0.01	0.08	0.01
25	TRANS 2- BUTENE	21.58	15.54	21.56	15.85	21.66	16.17
	BUTENE-1	31.20	9.07	31.25	9.27	31.02	9.46
	ISOBUTYLENE	0.48	28.56	0.50	28.60	0.49	28.37
30	CIS 2-BUTENE	15.71	11.26	15.65	11.46	15.84	11.67
	1,3 BUTADIENE	0.00	0.01	0.00	0.01	0.00	0.01
	HEAVIES (C5+)	0.01	3.53	0.00	2.90	0.00	2.41

35 FIG. 5 is a graph of the conversion and selectivity wt% versus run time depicting the results of this example. FIG. 6 is a graph of isobutylene yield and isobutylene wt% over run time for the results of this example. Surprisingly, the selectivities achieved with this pressed powder catalyst were better than the selectivities resulting from the same catalyst with binder run at similar isomerizing conditions; see, e.g., Example 11.

40 EXAMPLE 16

CATALYST: H-FERRIERITE NO. 5
 CATALYST CHARGE: 75.71 grams
 PRESSURE : 14.7 - 15.1 psia
 45 INLET TEMPERATURE: 430°C
 WHSV: 7

	COMPONENTS	FEED @ 2.4 HRS wt %	EFF @ 2.4 HRS wt %	FEED @ 12 HRS wt %	EFF @ 12 HRS wt %	FEED @ 24 HRS wt %	EFF @ 24 HRS wt %
5	METHANE	0.00	0.03	0.00	0.01	0.00	0.01
10	ETHANE	0.00	0.04	0.00	0.02	0.00	0.01
15	ETHYLENE	0.00	0.60	0.00	0.14	0.00	0.05
20	PROPANE	0.00	0.48	0.00	0.09	0.00	0.02
25	CYCLO PROPANE	0.00	0.00	0.00	0.00	0.00	0.00
30	PROPYLENE	0.01	9.29	0.01	3.84	0.01	1.64
	ISO-BUTANE	3.27	3.43	3.25	3.21	3.25	3.16
	N-BUTANE	19.70	18.33	19.73	19.79	19.73	19.83
	METHYL CYC- PROPANE	0.08	0.00	0.08	0.01	0.08	0.01
	TRANS 2- BUTENE	18.60	8/08	16.68	14.68	16.68	17.82
	BUTENE-1	46.17	4.47	46.04	8.19	46.04	9.96
	ISOBUTYLENE	0.90	14.29	0.88	24.23	0.88	25.53
	CIS 2-BUTENE	10.99	5.81	11.07	10.53	11.07	12.76
	1,3 BUTADIENE	0.06	0.01	0.06	0.01	0.06	0.01
	HEAVIES (C5+)	0.00	34.95	2.01	15.08	2.01	8.95

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EXAMPLE 16 (Continued)

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	COMPONENTS	FEED @ 36 HRS wt %	EFF @ 36 HRS wt %	FEED @ 48 HRS wt %	EFF @ 48 HRS wt %
10	METHANE	0.00	0.01	0.00	0.00
	ETHANE	0.00	0.01	0.00	0.00
	ETHYLENE	0.00	0.02	0.00	0.01
15	PROPANE	0.00	0.01	0.00	0.00
	CYCLO PROPANE	0.00	0.00	0.00	0.00
	PROPYLENE	0.01	0.67	0.01	0.34
20	ISO-BUTANE	3.24	3.09	3.24	3.07
	N-BUTANE	19.73	19.81	19.73	19.62
	METHYL CYC- PROPANE	0.08	0.01	0.08	0.01
25	TRANS 2- BUTENE	18.76	21.29	18.76	23.84
	BUTENE-1	45.95	12.15	45.95	13.84
30	ISOBUTYLENE	0.88	21.82	0.88	17.90
	CIS 2-BUTENE	11.10	15.30	11.10	17.19
	1,3 BUTADIENE	0.06	0.01	0.06	0.02
	HEAVIES (C5+)	0.00	5.59	0.00	3.93

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EXAMPLE 17

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CATALYST: H-FERRIERITE NO. 3
 CATALYST CHARGE: 75.71 grams
 PRESSURE: 14.6 - 15.2 psia
 INLET TEMPERATURE: 430°C
 45 WHSV: 7

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	COMPONENTS	FEED @ 3.3 HRS wt %	EFF @ 3.3 HRS wt %	FEED @ 12 HRS wt %	EFF @ 12 HRS wt %	FEED @ 24 HRS wt %	EFF @ 24 HRS wt %
5	METHANE	0.00	0.03	0.01	0.03	0.02	0.03
	ETHANE	0.00	0.03	0.00	0.03	0.00	0.02
	ETHYLENE	0.00	0.27	0.00	0.17	0.00	0.12
10	PROPANE	0.00	0.14	0.00	0.07	0.00	0.04
	CYCLO PROPANE	0.00	0.00	0.00	0.00	0.00	0.00
15	PROPYLENE	0.00	2.56	0.00	1.71	0.00	1.25
	ISO-BUTANE	2.84	2.95	2.83	2.88	2.85	2.90
	N-BUTANE	27.97	28.96	27.98	28.83	27.98	28.67
20	METHYL CYC- PROPANE	0.08	0.01	0.08	0.01	0.08	0.01
	TRANS 2- BUTENE	21.61	13.66	21.59	14.42	21.58	14.86
	BUTENE-1	30.90	7.77	30.91	8.33	30.95	8.59
25	ISOBUTYLENE	0.51	25.60	0.50	27.04	0.50	28.39
	CIS 2-BUTENE	15.87	9.82	15.89	10.41	15.84	10.72
30	1,3 BUTADIENE	0.00	0.01	0.00	0.01	0.00	0.01
	HEAVIES (C5+)	0.00	08.01	0.00	5.88	0.00	4.73

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EXAMPLE 17 (Continued)

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	COMPONENTS	FEED @ 48 HRS wt %	EFF @ 48 HRS wt %	FEED @ 72 HRS wt %	EFF @ 72 HRS wt %	FEED @ 96 HRS wt %	EFF @ 96 HRS wt %
10	METHANE	0.01	0.01	0.01	0.01	0.01	0.01
	ETHANE	0.00	0.02	0.00	0.01	0.00	0.01
	ETHYLENE	0.00	0.07	0.00	0.05	0.00	0.03
15	PROPANE	0.00	0.02	0.00	0.01	0.00	.01
	CYCLO PROPANE	0.00	0.00	0.00	0.00	0.00	0.00
	PROPYLENE	0.00	0.80	0.00	0.55	0.00	0.36
20	ISO-BUTANE	2.82	2.82	2.84	2.84	2.80	2.82
	N-BUTANE	27.97	28.92	27.94	28.51	27.96	28.46
	METHYL CYC- PROPANE	0.07	0.01	0.08	0.01	0.08	0.01
25	TRANS 2- BUTENE	21.59	15.58	21.60	15.84	21.63	16.61
	BUTENE-1	30.90	9.07	30.95	9.29	30.82	9.81
30	ISOBUTYLENE	0.51	28.94	0.51	28.80	0.51	27.98
	CIS 2-BUTENE	15.91	11.21	15.88	11.53	15.96	12.10
	1,3 BUTADIENE	0.00	0.01	0.00	0.01	0.00	0.01
35	HEAVIES (C5+)	0.01	2.32	0.00	2.36	0.00	1.61

40 EXAMPLE 18

CATALYST: H-FERRIERITE NO. 4
 CATALYST CHARGE: 97.73 grams
 PRESSURE: 14.7 - 15.2 psia
 45 INLET TEMPERATURE: 430°C
 WHSV: 7

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	COMPONENTS	FEED @ 3.3 HRS wt %	EFF @ 3.3 HRS wt %	FEED @ 12 HRS wt %	EFF @ 12 HRS wt %	FEED @ 24 HRS wt %	EFF @ 24 HRS wt %
5	METHANE	0.02	0.03	0.02	0.01	0.02	0.01
	ETHANE	0.00	0.02	0.00	0.00	0.00	0.00
10	ETHYLENE	0.00	0.22	0.00	0.05	0.00	0.03
	PROPANE	0.00	0.08	0.00	0.01	0.00	0.00
15	CYCLO PROPANE	0.00	0.00	0.00	0.00	0.00	0.00
	PROPYLENE	0.00	2.13	0.00	0.72	0.00	0.35
20	ISO-BUTANE	3.20	3.02	3.20	3.06	3.20	3.03
	N-BUTANE	23.0	22.44	23.0	22.88	23.0	22.96
25	METHYL CYC- PROPANE	0.08	0.01	0.08	0.01	0.08	0.01
	TRANS 2- BUTENE	19.5	14.43	19.5	16.52	19.5	17.07
30	BUTENE-1	39.90	8.84	39.90	9.67	39.90	10.00
	ISOBUTYLENE	0.80	26.54	0.80	29.41	0.80	30.08
	CIS 2-BUTENE	13.20	10.78	13.20	12.02	13.20	12.43
	1,3 BUTADIENE	0.01	0.01	0.01	0.01	0.01	0.01
	HEAVIES (C5+)	0.00	11.21	0.00	5.37	0.00	3.74

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EXAMPLE 18 (Continued)

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	COMPONENTS	FEED @ 48 HRS wt %	EFF @ 48 HRS wt %	FEED @ 72 HRS wt %	EFF @ 72 HRS wt %	FEED @ 96 HRS wt %	EFF @ 96 HRS wt %
10	METHANE	0.02	0.01	0.02	0.01	0.02	0.02
	ETHANE	0.00	0.00	0.00	0.00	0.00	0.00
	ETHYLENE	0.00	0.02	0.00	0.02	0.00	0.02
15	PROPANE	0.00	0.00	0.00	0.00	0.00	0.00
	CYCLO PROPANE	0.00	0.00	0.00	0.00	0.00	0.00
	PROPYLENE	0.00	0.22	0.00	0.16	0.00	0.13
20	ISO-BUTANE	3.20	3.06	3.20	3.04	3.20	3.07
	N-BUTANE	23.0	22.88	23.0	22.82	23.0	22.87
	METHYL CYC- PROPANE	0.08	0.01	0.08	0.01	0.08	0.01
25	TRANS 2- BUTENE	19.5	17.31	19.50	17.44	19.50	17.79
	BUTENE-1	39.90	10.47	39.90	10.63	39.90	10.80
	ISOBUTYLENE	0.08	29.88	0.08	29.64	0.08	29.34
30	CIS 2-BUTENE	13.20	12.68	13.20	12.83	13.20	13.01
	1,3 BUTADIENE	0.01	0.01	0.01	0.01	0.01	0.01
	HEAVIES (C5+)	0.00	3.18	0.00	3.12	0.00	2.68

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EXAMPLE 19

CATALYST: H-FERRIERITE NO. 6
 CATALYST CHARGE: 97.7 grams
 45 PRESSURE: 14.7 - 15.3 psia
 INLET TEMPERATURE: 430°C
 WHSV: 7

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	COMPONENTS	FEED @ 4.5 HRS wt %	EFF @ 4.5 HRS wt %	FEED @ 9 HRS wt %	EFF @ 9 HRS wt %	FEED @ 12 HRS wt %	EFF @ 12 HRS wt %
5	METHANE	0.01	0.01	0.01	0.01	0.01	0.01
	ETHANE	0.00	0.01	0.00	0.01	0.00	0.01
	ETHYLENE	0.00	0.11	0.00	0.09	0.00	0.08
10	PROPANE	0.00	0.13	0.00	0.10	0.00	0.08
	CYCLO PROPANE	0.00	0.00	0.00	0.00	0.00	0.00
15	PROPYLENE	0.00	1.47	0.00	1.39	0.00	1.24
	ISO-BUTANE	3.20	2.09	3.20	2.28	3.20	2.21
	N-BUTANE	23.04	16.06	23.04	17.72	23.04	17.39
20	METHYL CYC- PROPANE	0.08	0.00	0.08	0.01	0.08	0.00
	TRANS 2- BUTENE	19.53	9.13	19.53	10.54	19.53	10.56
	BUTENE-1	39.76	4.52	39.76	5.29	39.76	5.29
25	ISOBUTYLENE	0.80	17.34	0.80	19.95	0.80	19.84
	CIS 2-BUTENE	13.32	6.50	13.32	7.52	13.32	7.57
	1,3 BUTADIENE	0.01	0.00	0.01	0.00	0.01	0.00
30	HEAVIES (C5+)	0.00	42.45	0.00	34.89	0.00	35.52

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EXAMPLE 19 (Continued)

	COMPONENTS	FEED @ 16 HRS wt %	EFF @ 16 HRS wt %	FEED @ 21 HRS wt %	EFF @ 21 HRS wt %	FEED @ 26 HRS wt %	EFF @ 26 HRS wt %
5	METHANE	0.01	0.01	0.01	0.01	0.01	0.01
10	ETHANE	0.00	0.01	0.00	0.01	0.00	0.01
	ETHYLENE	0.00	0.07	0.00	0.07	0.00	0.06
	PROPANE	0.00	0.08	0.00	0.07	0.00	0.06
15	CYCLO PROPANE	0.00	0.00	0.00	0.00	0.00	0.00
	PROPYLENE	0.00	1.24	0.00	1.22	0.00	1.17
	ISO-BUTANE	3.20	2.39	3.20	2.50	3.20	2.57
20	N-BUTANE	23.04	18.23	23.04	19.40	23.04	.20
	METHYL CYC- PROPANE	0.08	0.00	0.08	0.00	0.08	0.00
25	TRANS 2- BUTENE	19.53	11.24	19.53	12.14	19.53	12.67
	BUTENE-1	39.76	5.70	39.76	6.18	39.76	6.46
	ISOBUTYLENE	0.80	21.19	0.80	22.78	0.80	23.71
30	CIS 2-BUTENE	13.32	8.03	13.32	8.65	13.32	9.07
	1,3 BUTADIENE	0.01	0.00	0.01	0.00	0.01	0.00
	HEAVIES (C5+)	0.00	31.62	0.00	26.77	0.00	23.98

35 EXAMPLE 20

CATALYST: SAPO-11 (Provided by Union Carbide Corporation)
 CATALYST CHARGE: 400 grams
 INLET TEMPERATURE: 300°C
 40 PRESSURE: 17-20 psia
 WHSV: 1-2

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	COMPONENTS	FEED wt %	EFF @ 1.5 HRS wt %	EFF @ 4.7 HRS wt %	EFF @ 16.0 HRS wt %
5	METHANE	0.00	0.01	0.00	0.00
	ETHANE	0.00	0.01	0.00	0.00
10	ETHYLENE	0.00	0.08	0.03	0.01
	PROPANE	0.00	0.31	0.08	0.01
	CYCLO PROPANE	0.00	0.00	0.00	0.00
15	PROPYLENE	0.00	2.14	1.66	0.35
	ISO-BUTANE	2.61	3.66	2.15	2.93
	N-BUTANE	26.28	17.34	15.78	20.83
20	METHYL CYC- PROPANE	0.06	0.00	0.00	0.00
	TRANS 2-BUTENE	13.61	3.32	8.01	20.84
	BUTENE-1	48.67	1.44	3.62	10.23
25	ISOBUTYLENE	0.42	6.05	10.12	5.93
	CIS 2-BUTENE	6.90	2.29	5.71	14.88
	1,3 BUTADIENE	1.26	0.00	0.00	0.06
30	HEAVIES (C5+)	0.18	63.35	52.85	23.92

EXAMPLE 21

35 CATALYST: SAPO-11 (REGENERATED)*
 CATALYST CHARGE: 97.70 grams
 PRESSURE: 27 psia
 WHSV: 15

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	COMPONENTS	FEED wt %	EFF @ 400° C & 4 HRS wt %	EFF @ 410° C & 13 HRS wt %
5	METHANE	0.00	0.01	0.00
10	ETHANE	0.01	0.01	0.01
	ETHYLENE	0.86	0.80	0.92
15	PROPANE	0.00	0.00	0.00
	CYCLO PROPANE	0.00	0.00	0.00
	PROPYLENE	0.12	62.07	0.81
	ISO-BUTANE	0.00	0.19	0.08
20	N-BUTANE	0.04	0.94	0.70
	METHYL CYC-PROPANE	0.00	0.00	0.00
	TRANS 2-BUTENE	57.88	30.26	36.47
	BUTENE-1	10.74	16.51	19.31
25	ISOBUTYLENE	0.00	15.85	11.10
	CIS 2-BUTENE	30.26	21.79	626.61
	1,3 BUTADIENE	0.01	0.13	0.16
	HEAVIES (CS+)	0.08	11.44	3.83

30 * The SAPO-11 catalyst was regenerated by heating it to 500°C in a muffle furnace.

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Examples 22-24 show experimental results using the larger pore hydrogen mordenite. In comparison, Examples 25 and 26 show experimental results reflecting improved results of isobutylene selectivities using the smaller pore magnesium mordenite.

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EXAMPLE 22

CATALYST:	HYDROGEN MORDENITE
CATALYST CHARGE:	97.70 grams
PRESSURE:	22-26 psia
WHSV:	15

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	COMPONENTS	FEED wt %	EFF @ 0.3 HRS & 327° C wt %	EFF @ 2.6 HRS & 347 C wt %
5	METHANE	0.00	0.00	0.01
10	ETHANE	0.01	0.02	0.02
	ETHYLENE	0.86	0.76	1.11
	PROPANE	0.00	0.09	0.03
15	CYCLO PROPANE	0.00	0.00	0.00
	PROPYLENE	0.12	1.97	1.79
	ISOBUTANE	0.00	0.35	0.19
	N-BUTANE	0.04	1.04	1.10
20	METHYL CYC-PROPANE	0.00	0.00	0.00
	TRANS 2-BUTENE	57.88	25.20	32.40
	BUTENE-1	10.74	14.39	18.12
25	ISOBUTYLENE	0.00	2.51	1.17
	CIS 2-BUTENE	30.26	18.12	23.60
	1,3 BUTADIENE	0.01	0.00	0.00
30	HEAVIES (C5+)	0.08	35.56	20.48

EXAMPLE 23

35 CATALYST: HYDROGEN MORDENITE
 CATALYST CHARGE: 97.70 grams
 PRESSURE: 17-19 psia
 WHSV: 14

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	COMPONENTS	FEED wt %	@ 3 HRS & 400° C wt %	@ 5 HRS & 405° C wt %	@ 7 HRS & 423° C wt %	@ 8.6 HRS & 419° C wt %
5	METHANE	0.04	0.03	0.03	0.03	0.03
10	ETHANE	0.00	0.00	0.00	0.00	0.00
15	ETHYLENE	0.00	0.01	0.00	0.00	0.00
20	PROPANE	0.00	0.00	0.00	0.00	0.00
25	CYCLO PROPANE	0.00	0.00	0.00	0.00	0.00
30	PROPYLENE	0.00	0.41	0.30	0.26	0.23
	ISO-BUTANE	3.29	3.24	3.26	3.24	3.25
	N-BUTANE	21.09	21.04	21.02	21.02	21.04
	METHYL CYC- PROPANE	0.06	0.00	0.00	0.00	0.00
	TRANS 2-BUTENE	23.64	30.91	31.56	31.41	31.64
	BUTENE-1	34.13	17.48	17.22	17.77	17.74
	ISOBUTYLENE	0.25	1.57	1.28	1.28	1.15
	CIS 2-BUTENE	17.39	22.44	22.68	22.77	22.86
	1,3 BUTADIENE	0.00	0.01	0.01	0.01	0.01
	HEAVIES (C5+)	0.10	2.87	2.65	2.22	2.05

EXAMPLE 24

CATALYST: M-8 HYDROGEN MORDENITE
 CATALYST CHARGE: 97.70 grams
 40 PRESSURE : 23-29 psia
 WHSV: 15

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	COMPONENTS	FEED wt %	EFF @ 0.1 HRS & 317° C wt %	EFF @ 5.0 HRS & 224° C wt %
5	METHANE	0.00	0.00	0.00
10	ETHANE	0.01	0.02	0.01
15	ETHYLENE	0.86	0.82	0.76
20	PROPANE	0.00	0.19	0.02
25	CYCLO PROPANE	0.00	0.00	0.00
30	PROPYLENE	0.12	1.33	1.30
35	ISO-BUTANE	0.00	0.46	0.15
40	N-BUTANE	0.04	1.12	0.75
45	METHYL CYC-PROPANE	0.00	0.00	0.00
50	TRANS 2-BUTENE	57.88	30.06	32.86
55	BUTENE-1	10.74	14.28	18.95
60	ISOBUTYLENE	0.00	2.22	1.05
65	CIS 2-BUTENE	30.26	21.11	23.16
70	1,3 BUTADIENE	0.01	0.00	0.00
75	HEAVIES (C5+)	0.08	28.38	20.99

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EXAMPLE 25

CATALYST: MAGNESIUM-MORDENITE
 40 CATALYST CHARGE: 96 grams
 PRESSURE: 26-32 psia
 INLET TEMPERATURE: 320° C
 WHSV: 15

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	COMPONENTS	FEED wt %	EFF @ 0.2 HRS wt %	EFF @ 2.0 HRS wt %
5	METHANE	0.00	0.00	0.01
	ETHANE	0.01	0.04	0.05
10	ETHYLENE	0.86	0.44	1.08
	PROPANE	0.00	0.00	0.00
	CYCLO PROPANE	0.00	0.00	0.00
	PROPYLENE	0.12	0.96	2.04
15	ISO-BUTANE	0.00	0.19	0.25
	N-BUTANE	0.04	0.67	0.85
	METHYL CYC-PROPANE	0.00	0.00	0.00
20	TRANS 2-BUTENE	57.88	30.05	36.57
	BUTENE-1	10.74	6.25	19.97
	ISOBUTYLENE	0.00	10.59	3.38
25	CIS 2-BUTENE	30.26	20.87	29.71
	1,3 BUTADIENE	0.01	0.00	0.00
	HEAVIES (C5+)	0.08	29.94	6.09

30 EXAMPLE 26

CATALYST: MAGNESIUM MORDENITE
 CATALYST CHARGE: 97.73 grams
 PRESSURE: 19-20 psia
 35 INLET TEMPERATURE: 348° C
 WHSV: 15

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	COMPONENTS	FEED wt %	EFF @ 0.2 HRS	EFF @ 2.6 HRS
5	METHANE	0.00	0.01	0.00
	ETHANE	0.01	0.02	0.01
	ETHYLENE	0.86	0.12	0.13
10	PROPANE	0.00	0.00	0.00
	CYCLO PROPANE	0.00	0.00	0.00
	PROPYLENE	0.12	2.16	1.19
15	ISO-BUTANE	0.00	0.28	0.12
	N-BUTANE	0.04	0.79	0.69
	METHYL CYC-PROPANE	0.00	0.00	0.00
	TRANS 2-BUTENE	57.88	32.24	38.09
20	BUTENE-1	10.74	18.79	19.54
	ISOBUTYLENE	0.00	4.47	2.29
	CIS 2-BUTENE	30.26	22.52	27.25
25	1,3 BUTADIENE	0.01	0.00	0.00
	HEAVIES (C5+)	0.08	18.60	10.69

30 The following Examples 27-29 show experimental results of isopentene conversion using a 1-pentene feed.
 The testing apparatus and procedure were the same as described earlier for the n-pentene stream.

EXAMPLE 27

35 CATALYST: H-FERRIERITE NO. 1
 CATALYST CHARGE: 30 grams of extrudate diluted to 240 cc with alundum
 PRESSURE: 1 atm
 FEED: 1-pentene

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5	Sample Start Time	1.7 hrs	3.2 hrs	4.8 hrs	6.2 hrs
	Sample Stop Time	2.3 hrs	3.7 hrs	5.3 hrs	7.4 hrs
	WHSV (1/hr)	7.1	7.1	7.1	4.0
	Average Temp	416°C	401°C	430°C	430°C
10	C4-	7.6	8.9	8.1	10.3
	3-methyl-1-butene	3.6	4.0	4.1	2.9
	trans-2-pentene	13.4	12.9	13.5	13.9
15	2-methyl-2-butene	42.1	41.1	40.6	41.0
	1-pentene	4.3	4.3	4.7	3.7
	2-methyl-1-butene	20.4	20.9	21.3	18.9
20	cis-2-pentene	6.8	6.5	7.0	7.6
	C6+	1.8	1.4	0.7	1.7
25	isoamylenes (2m1b + 2m2b)	62.5	62.0	61.9	59.9

EXAMPLE 28

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CATALYST: H-FERRIERITE NO. 1
 CATALYST CHARGE: 30 grams of extrudate diluted to 240 cc with alundum
 PRESSURE: 1atm
 FEED: 1-pentene

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5	Sample Start Time	1.3 hrs	2.9 hrs	3.8 hrs	4.7 hrs
	Sample Stop Time	1.6 hrs	3.2 hrs	4.1 hrs	5.0 hrs
	WHSV (l/hr)	10.0	13.0	16.0	10.0
	Average Temp	417°C	416°C	414°C	421°C
10	C4-	7.5	2.6	1.9	5.3
	3-methyl-1-butene	4.3	3.3	2.9	4.5
	trans-2-pentene	13.2	14.6	14.9	13.9
	2-methyl-2-butene	41.3	45.8	47.0	42.3
15	1-pentene	4.6	4.4	4.3	4.8
	2-methyl-1-butene	21.6	21.1	20.4	21.8
	cis-2-pentene	6.8	7.5	7.7	6.9
20	C6+	0.9	0.6	0.9	0.6
	isoamylenes (2m1b + 2m2b)	62.9	66.9	67.4	64.1

25 EXAMPLE 29

CATALYST: H-FERRIERITE NO. 1
 CATALYST CHARGE: 10 grams of extrudate diluted to 240 cc with alundum
 30 PRESSURE: 1 atm
 FEED: 1-pentene

35	Sample Start Time	1.1 hrs	2.4 hrs	3.4 hrs	4.3 hrs
	Sample Stop Time	1.8 hrs	3.1 hrs	3.9 hrs	4.7 hrs
	WHSV (l/hr)	16.0	19.0	22.0	25.0
	Average Temp	421°C	422°C	421°C	421°C
40	C4-	3.3	5.5	2.3	1.3
	3-methyl-1-butene	2.6	4.1	3.2	3.0
	trans-2-pentene	15.1	14.4	16.5	17.1
45	2-methyl-2-butene	46.9	42.3	44.2	44.4
	1-pentene	4.2	5.0	5.5	5.7
	2-methyl-1-butene	19.2	21.2	20.2	19.3
50	cis-2-pentene	7.8	7.3	8.2	8.8
	C6+	1.0	0.2	0.1	0.5
	isoamylenes (2m1b + 2m2b)	66.1	63.5	64.4	63.7

5	5.1 hrs 5.7 hrs 16.0 414°C	18.6 hrs 18.9 hrs 16.0 414°C	24.0 hrs 24.4 hrs 16.0 414°C	30.7 hrs 30.9 hrs 16.0 415°C	37.4 hrs 37.8 hrs 16.0 415°C	50.1 50.5 16.0 414°C
10	2.6	1.2	1.3	0.7	1.0	0.8
15	3.3	2.8	3.0	2.5	2.4	2.3
20	15.7	18.2	20.3	22.7	24.0	26.8
	44.7	42.7	38.8	35.9	33.8	24.3
	5.3	6.3	8.2	9.6	11.1	19.6
	20.3	18.5	18.1	16.6	15.4	12.6
	8.1	9.4	10.3	11.5	12.1	13.7
	0.1	0.9	0.0	0.3	0.0	0.0
	65.0	61.2	56.9	52.5	49.2	36.9

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Schematic Flow Chart

FIG. 7 depicts a flow scheme for producing an alkyl-tert-alkyl-ether, particularly methyl-tert-butyl-ether (MTBE) by means of first isomerizing n-butene to isobutylene, separating out an isobutylene stream for further processing to produce MTBE. In the flow scheme, a hydrocarbon stream containing butylene is charged to an isomerization zone 4, via conduit 2. The hydrocarbon stream can be charged continuously. As the butylene feed enters the isomerization zone, it is preferentially vaporized to a gaseous phase. The isomerization zone 4 contains an isomerizing catalyst, preferably the hydrogen form of ferrierite. The isomerization zone is further maintained at isomerizing conditions so as to maximize the structural isomerization of butylene to isobutylene. The effluent from the isomerization zone 4 containing isobutylene is passed through conduit 6 to a separation zone 8. Optionally, the isomerizing catalyst can be regenerated in the isomerization zone 4.

The separation zone 8 is maintained under conditions sufficient to maximize separation of isobutylene from the lighter olefins, ethylene and propylene, and from the heavier olefins, aromatics and paraffins. The separation zone 8 can employ various means known in the art to effect separation of light, medium and heavy olefins, aromatics or paraffins. For example, the zone may comprise a series of adsorbent beds comprising molecular sieves as described in U.S. Patent Nos. 4,717,784 and 4,210,771, incorporated herein by reference. Or the separation zone may conveniently separate the light, medium and heavy fractions by distillation using processes well known in the art. The lighter olefins, ethylene and propylene, and lighter paraffins are removed via conduit 10. The higher paraffins and olefins, C₅ and above, and aromatics are removed via conduit 12. The butylene fraction, comprising isobutylene, is removed from the separation zone via conduit 14 to an MTBE reaction zone 16 containing an etherification catalyst. Thereafter, methanol is fed into the MTBE reaction zone 16 via conduit 18. The MTBE reaction process can be carried out in any one of a number of ways, such as for example taught by U. S. Patent No. 4, 876, 394, incorporated herein by reference. The MTBE effluent 20 is recovered preferably as a bottoms product and the unreacted butene/isobutylene stream is recovered and recycled via conduit 22 to the butylene feed at conduit 2.

Claims

- 55 1. A process for structurally isomerizing a linear olefin of at least 4 carbon atoms to its corresponding methyl branched isoolesfin, which process comprises contacting a hydrocarbon feed stream containing at least one said linear olefin with an isomerizing catalyst at a temperature of from 340°C to 650°C, said isomer-

izing catalyst comprising at least one zeolite with one or more one-dimensional pore structure having a pore size small enough to retard by-product dimerization and coke formation within the pore structure and large enough to permit entry of the linear olefin and allow formation and diffusion of the methyl branched isoolefin.

- 5 2. A process according to claim 1 wherein the zeolite has a pore size of from 0.42 to 0.7 nm in only one dimension.
- 10 3. A process according to claim 2 wherein the zeolite has a 10 member or puckered 12 member ring channel structure in one dimension and optionally has an 8 member or less ring channel structure in the other dimensions.
- 15 4. A process according to claim 1, 2 or 3 wherein the zeolite is selected from SAPO, MeAPO, MeAPSO, ELAPO, ELAPSO and ZSM zeolites.
- 20 5. A process according to claim 1, 2 or 3 wherein the zeolite is selected from ferrierite, the hydrogen form of ferrierite, SAPO-11, SAPO-31, SAPO-41, FU-9, NU-23, NU-10, ZSM-12, ZSM-22, ZSM-23, ZSM-35, ZSM-48, ZSM-50, MeAPO-11, MeAPO-31, MeAPO-41, MeAPSO-11, MeAPSO-31, MeAPSO-41, ELAPO-11, ELAPO-31, ELAPO-41, ELAPSO-11, ELAPSO-31, ELAPSO-41, laumontite, clinoptilolite, cancrinite, offretite, hydrogen form of heulandite, hydrogen form of stilbite, and the magnesium or calcium form of mordenite.
- 25 6. A process according to any one of the preceding claims wherein the linear olefin is at least one of 1-butene, cis-2-butene, trans-2-butene, 1-pentene, cis-2-pentene and trans-2-pentene.
- 30 7. A process according to any one of the preceding claims wherein the hydrocarbon feed stream comprises from 40 to 100 wt. % normal butene or normal pentene.
- 35 8. A process according to any one of the preceding claims wherein the zeolite is combined with a binder.
- 40 9. A process according to claim 8 wherein the binder is at least one of silica, silica-alumina, alumina, bentonite, kaolin, bentonite with alumina, montmorillonite, attapulgite, titania and zirconia.
- 45 10. A process according to any one of the preceding claims which is carried out at a temperature of from 340°C to 600°C, an olefin partial pressure of above 0.5 atmospheres, and a hydrocarbon based weight hourly space velocity of 1 to 50 hr⁻¹.
- 50 11. A process according to claim 10 wherein the temperature is from 340°C to 475°C.
- 55 12. A process according to claim 11 which is carried out at a temperature of from 370°C to 440°C, atmospheric pressure, and a hydrocarbon based weight hourly space velocity of 7 to 15 hr⁻¹.
- 60 13. A process according to any one of the preceding claims, which comprises the further steps of:-
 (i) passing the isomerization effluent to an etherification zone containing an alcohol and an etherification catalyst to form a reaction product comprising an alkyl-tert-alkyl-ether; and
 (ii) recovering the alkyl-tert-alkyl-ether reaction product.
- 65 14. A process according to claim 13 wherein the isomerization zone comprises a packed bed reactor, moving bed reactor, or fluidized bed reactor.

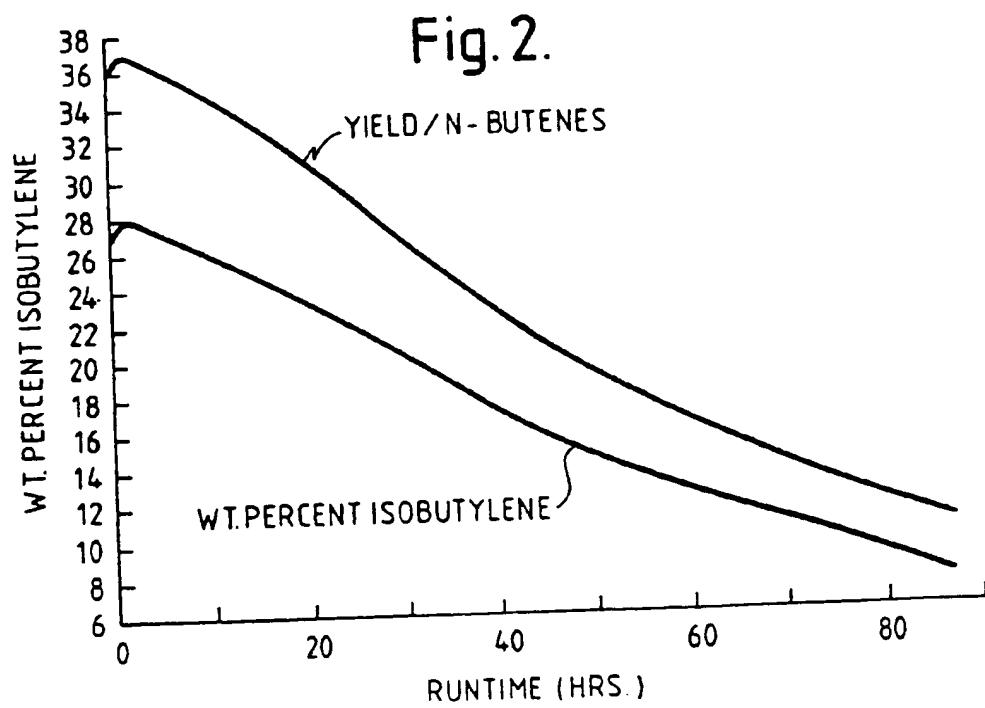
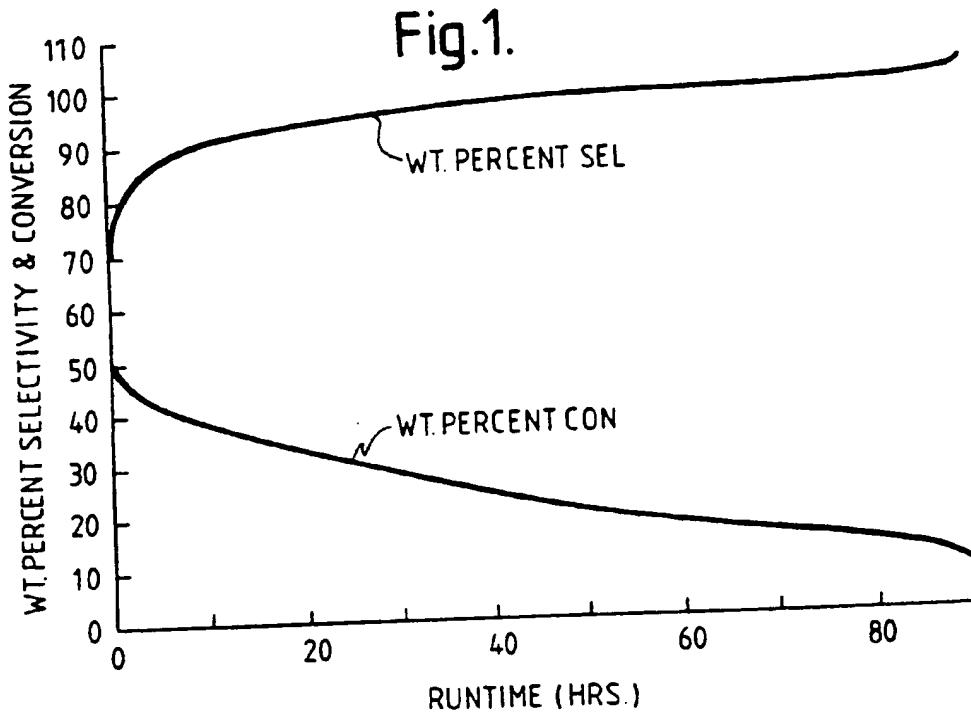


Fig. 3.

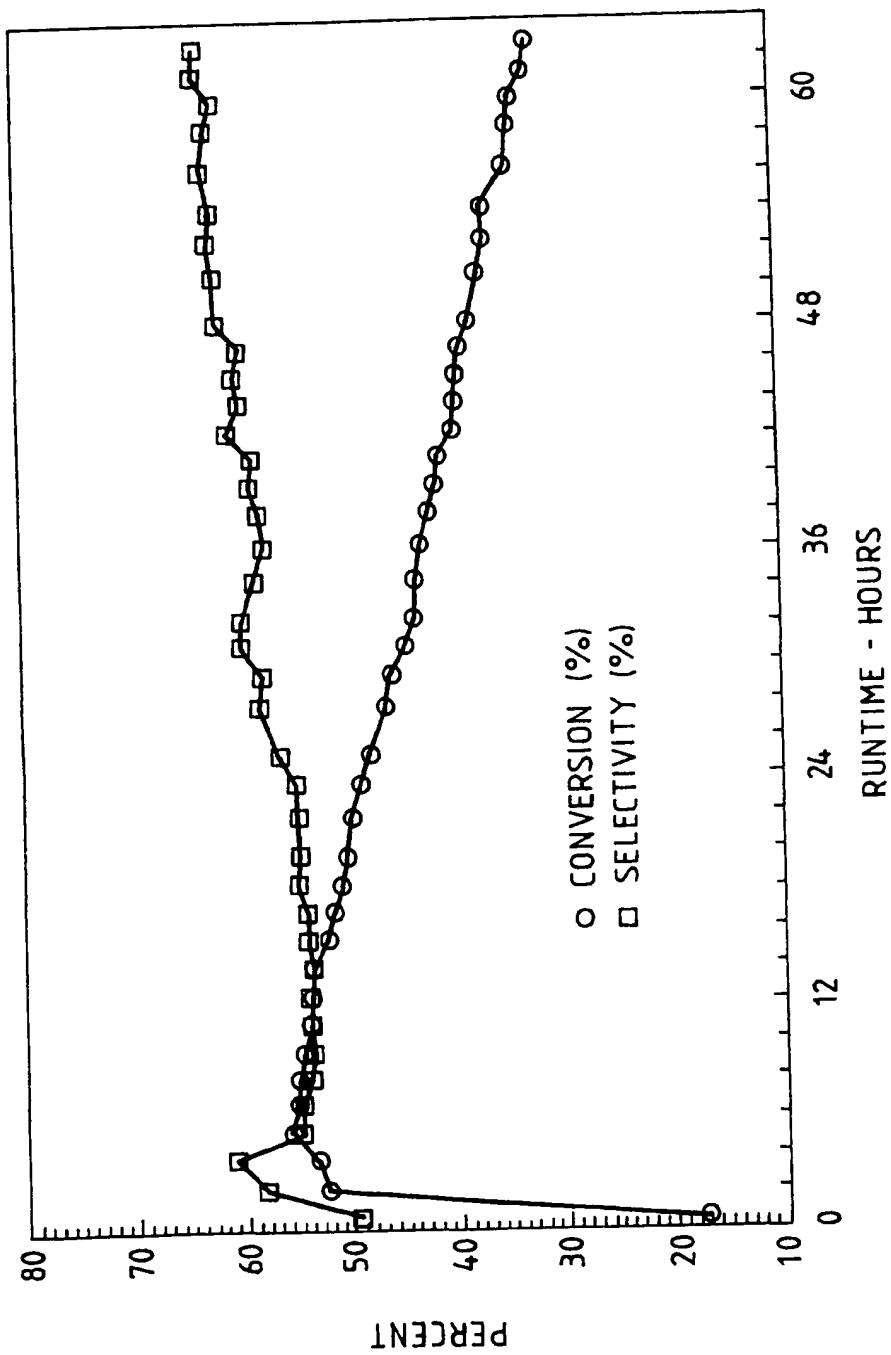


Fig. 4

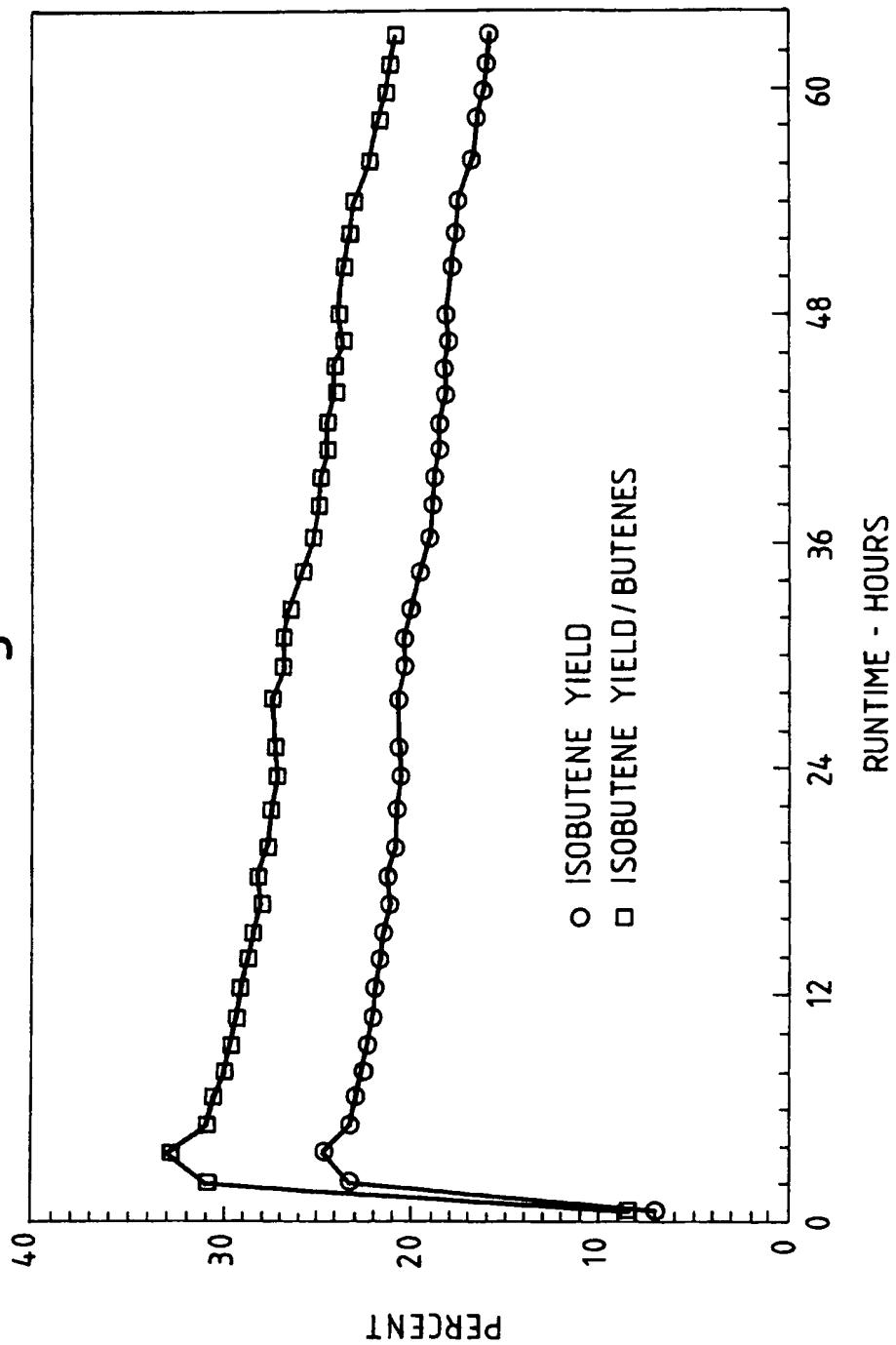


Fig. 5.

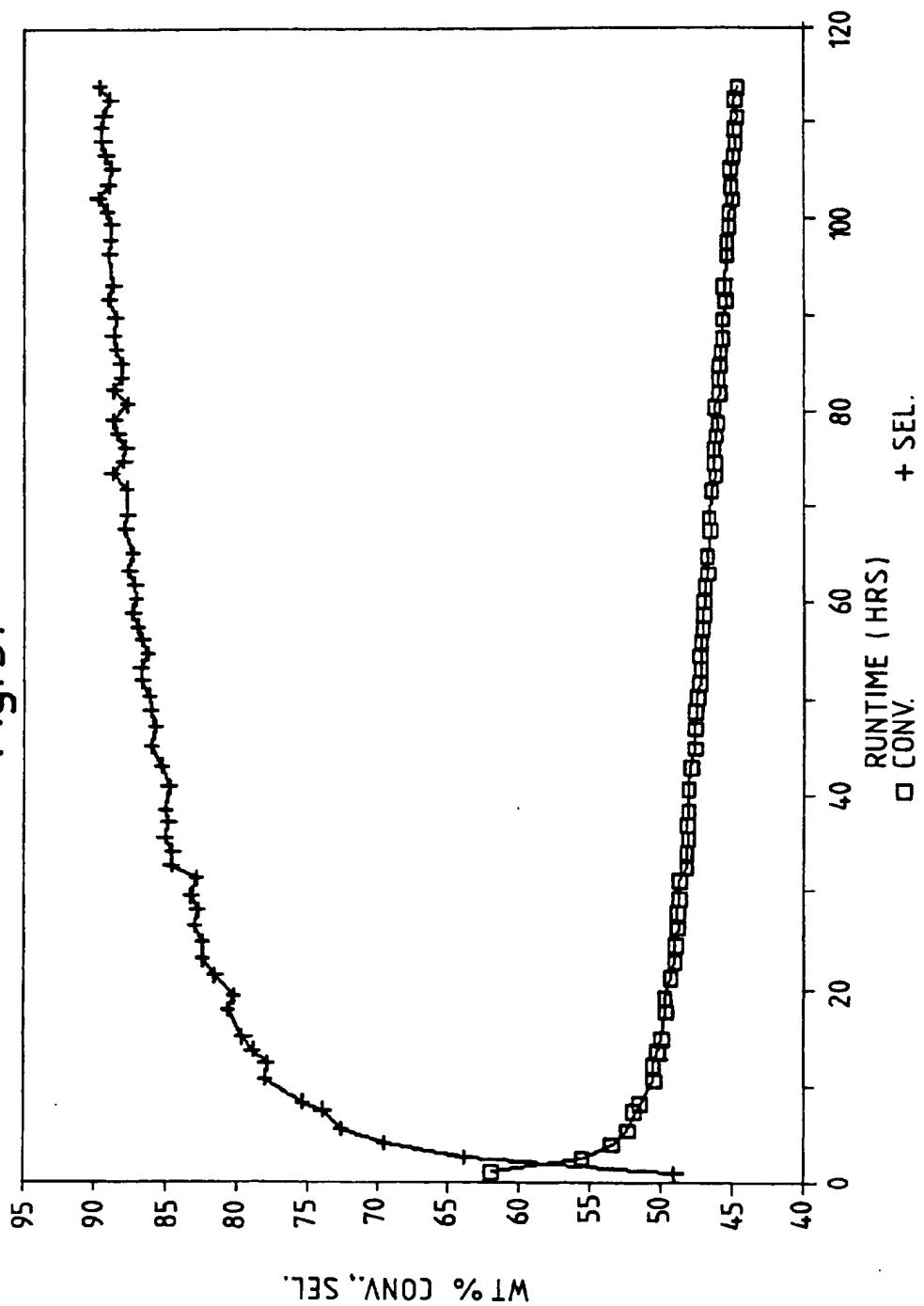


Fig. 6.

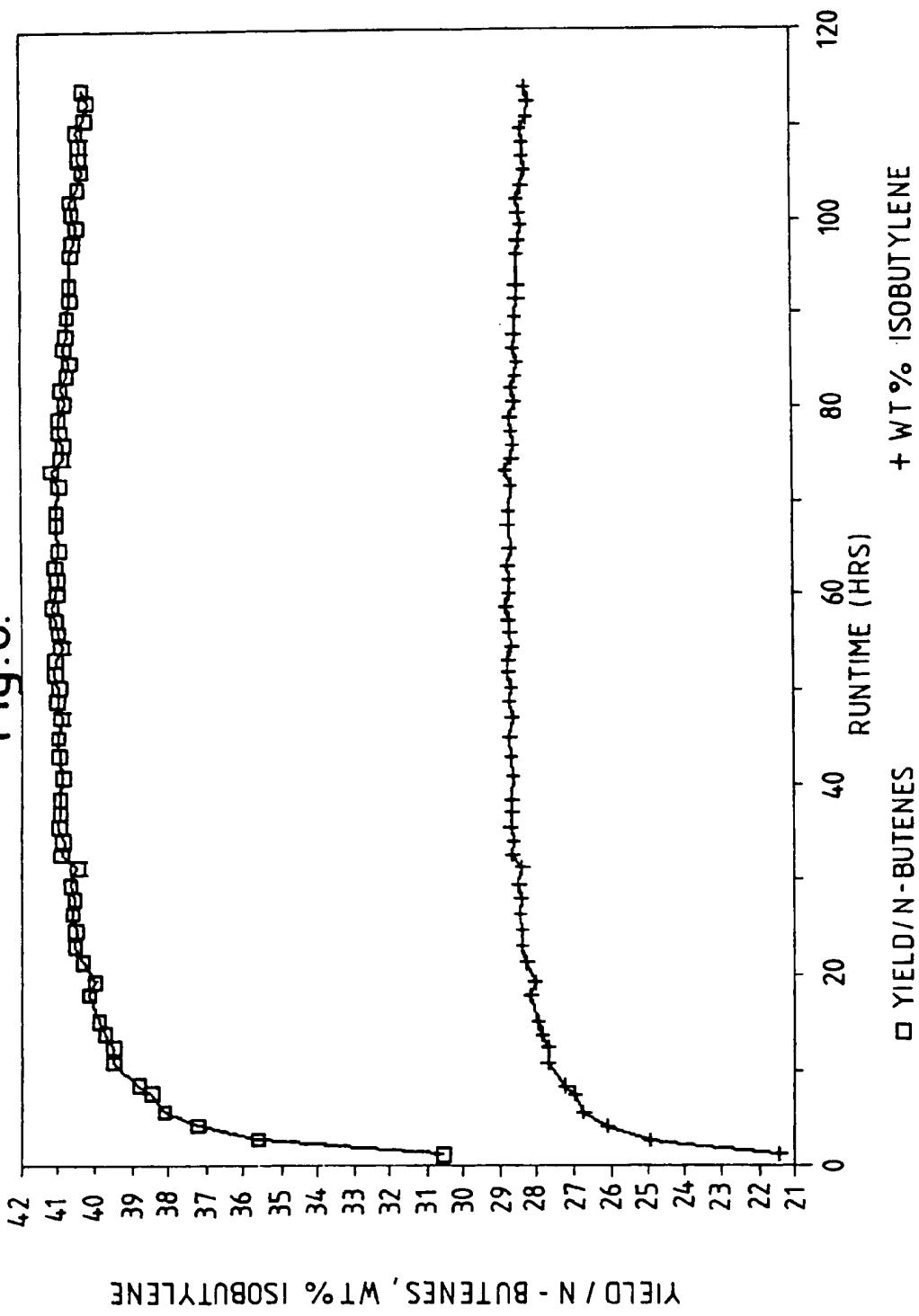
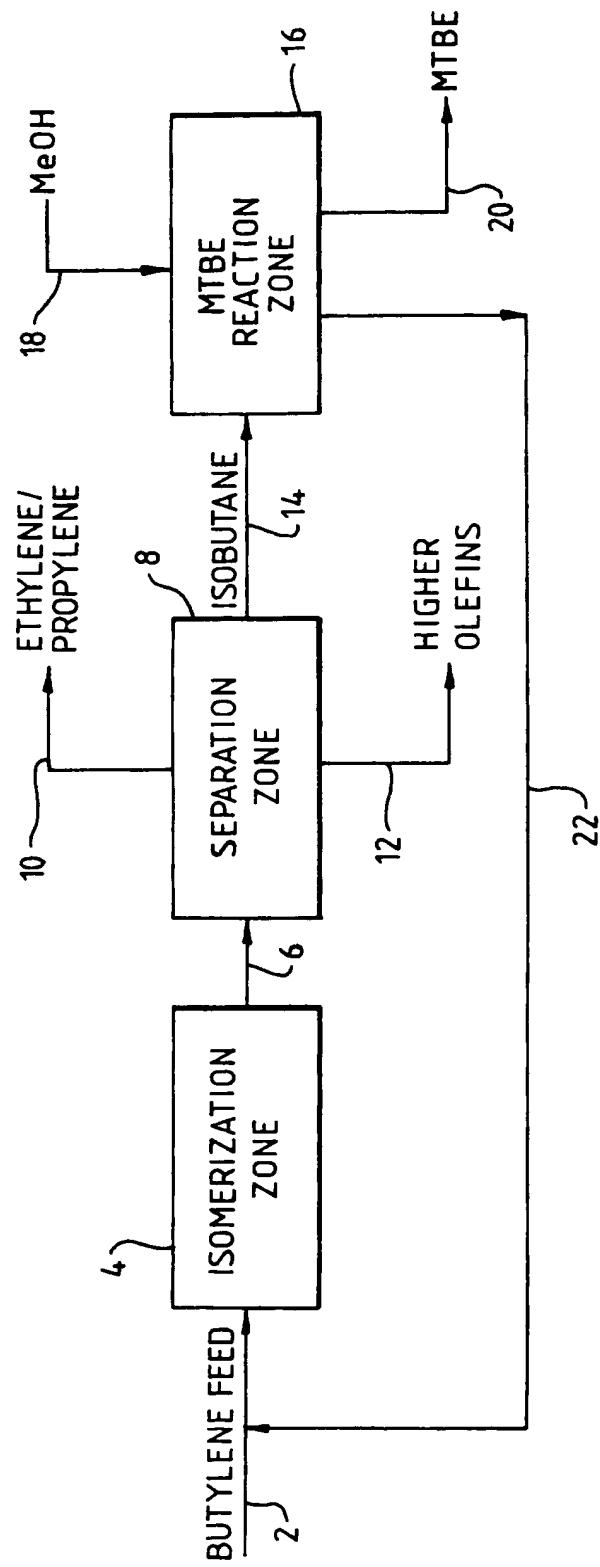


Fig. 7.





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(54) Process for isomerizing linear olefins to isoolefins.

(57) This invention provides a process to convert linear alkenes such as butene-1 and butene-2 to methyl branched chain alkenes such as isobutylene using one dimensional, medium pore zeolite catalysts and similar type catalysts such as SAPO's and MeAPOS's. The pore size for the catalyst should be greater than 0.42 nm and less than 0.7 nm, preferably with a larger dimension of between 0.5 and 0.6 nm. This pore size allows the branched chain alkenes to form and diffuse out of the catalyst while reducing the formation of unwanted by-products, including dimers, trimers, aromatics and coke. This invention has been demonstrated with H-ferrierite, SAPO-11, and magnesium mordenite in a laboratory scale reactor. Selectivities ranging from about 50% to almost 100% were demonstrated for isobutylene formation using H-ferrierite, at temperatures ranging from about 340°C to about 440°C.

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EUROPEAN SEARCH REPORT

Application Number

EP 92 30 5090 • C

DOCUMENTS CONSIDERED TO BE RELEVANT			
Category	Citation of document with indication, where appropriate, of relevant passages	Relevant to claim	CLASSIFICATION OF THE APPLICATION (Int. Cl.s)
A	EP-A-0 323 135 (MOBIL OIL CORPORATION) * abstract *	1	C07C5/23 C07C5/27
A	EP-A-0 111 808 (BAYER A.G.) * the whole document *	1	
A	EP-A-0 054 855 (E.C. ERDÖLCHEMIE GMBH) * abstract *	1	
A,P	US-A-5 091 590 (M.N. HARANDI ET AL.) * claims *	1	

			TECHNICAL FIELDS SEARCHED (Int. Cl.s)
			C07C
<p>The present search report has been drawn up for all claims</p>			
Place of search BERLIN	Date of completion of the search 10 MAY 1993	Examiner FRELON D.	
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